

Molecular Physics Division Fachverband Molekülphysik (MO)

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Overview of Invited Talks and Sessions

(lecture rooms HS 38.02 and HS 38.03; Poster.IV)

Invited Talks

MO 1.1	Mon	10:30–11:00	V38.03	Vibrational Molecular Interferometry — •HERMAN L OFFERHAUS, ERIK T GARBACIK, SHAUL MUKAMEL, ALEXANDER CW VAN RHIJN, CEES OTTO, JENNIFER L HEREK
MO 3.1	Mon	14:00–14:30	V38.02	Quantum chemical description of photo-induced molecular processes — •ANDREAS DREUW
MO 9.1	Tue	10:30–11:00	V38.03	The Interplay between Electron Transfer and Förster Resonant Energy Transfer — •IGOR PUGLIESI, PATRICK KÖLLE, REGINA DE VIVIE RIEDLE, HEINZ LANGHALS, EBERHARD RIEDLE
MO 12.1	Tue	14:00–14:30	V38.03	New insights into solution-phase chemistry under ambient conditions via ultrafast X-ray spectroscopy — •NILS HUSE
MO 17.1	Thu	10:30–11:00	V38.03	Ultrafast Processes in Single Molecules: from Small Chromophores to Photosynthetic Antenna Complexes — •RICHARD HILDNER, DAAN BRINKS, RICHARD J. COGDELL, NIEK F. VAN HULST
MO 18.1	Thu	14:00–14:30	V38.02	Excited-states and nonadiabatic dynamics: unveiling mechanistic aspects of ultrafast photoprocesses in nucleobases — •MARIO BARBATTI
MO 23.1	Fri	10:30–11:00	V38.03	A homonuclear polar molecule — •HOSSEIN SADEGHPOUR

Invited talks of the joint symposium SYRA

See SYRA for the full program of the Symposium.

SYRA 1.1	Tue	10:30–11:00	V47.01	Quantum optics and quantum information with Rydberg excited atoms. — •KLAUS MOLMER
SYRA 1.2	Tue	11:00–11:30	V47.01	Cooperative non-linear optics using Rydberg atoms — •CHARLES ADAMS
SYRA 2.1	Tue	14:00–14:30	V47.01	Ultralong-range Rydberg molecules — •THOMAS POHL
SYRA 2.2	Tue	14:30–15:00	V47.01	Quantum Information Processing with Rydberg Atoms — •PHILIPPE GRANGIER

Invited talks of the joint symposium SYIB

See SYIB for the full program of the Symposium.

SYIB 1.1	Tue	10:30–11:00	V55.22	Nuclear physics with stored highly-charged radioactive ions — •YURI LITVINOV
SYIB 1.2	Tue	11:00–11:30	V55.22	High Precision Laser Spectroscopy at the Storage Ring ESR — •WILFRIED NÖRTERSCHÄUSER
SYIB 1.3	Tue	11:30–12:00	V55.22	Storage-ring measurements of hyperfine-induced one-photon transitions in highly charged ions — •STEFAN SCHIPPERS
SYIB 1.4	Tue	12:00–12:30	V55.22	Low-Temperature Molecular Recombination from fast Electron and Ion Beams — •OLDRICH NOVOTNY

SYIB 2.1	Tue	14:00–14:30	V55.22	Ion induced fragmentation of large (bio)molecules — •THOMAS SCHLATHÖLTER
SYIB 2.2	Tue	14:30–15:00	V55.22	Using femtosecond lasers for determining the structure and dynamics of complex molecules — •JASON GREENWOOD
SYIB 2.3	Tue	15:00–15:30	V55.22	Fast beam momentum spectroscopy on XUV excited molecular ions — •HENRIK PEDERSEN
SYIB 2.4	Tue	15:30–16:00	V55.22	Electron Emission from Hot Stored Molecular and Cluster Anions — •MICHAEL LANGE, KLAUS BLAUM, CHRISTIAN BREITENFELDT, MICHAEL FROESE, SEBASTIAN MENK, ANDREAS WOLF, SWARUP DAS, MANAS MUKHERJEE

Sessions

MO 1.1–1.8	Mon	10:30–12:45	V38.03	Vibrational Spectroscopy
MO 2.1–2.7	Mon	10:30–12:15	V38.02	Electronic Spectroscopy
MO 3.1–3.7	Mon	14:00–16:00	V38.02	Quantum Chemistry
MO 4.1–4.8	Mon	14:00–16:00	V38.03	Cold Molecules I
MO 5.1–5.10	Mon	16:30–19:00	V38.02	Experimental Techniques
MO 6.1–6.10	Mon	16:30–19:00	V38.03	Femtosecond Spectroscopy I
MO 7.1–7.6	Tue	10:30–12:30	V47.01	SYRA: Ultracold Rydberg Atoms and Molecules 1
MO 8.1–8.8	Tue	10:30–12:30	V38.02	Photochemistry
MO 9.1–9.7	Tue	10:30–12:30	V38.03	Femtosecond Spectroscopy II
MO 10.1–10.6	Tue	14:00–16:00	V47.01	SYRA: Ultracold Rydberg Atoms and Molecules 2
MO 11.1–11.8	Tue	14:00–16:00	V38.02	Biomolecules
MO 12.1–12.7	Tue	14:00–16:00	V38.03	Femtosecond Spectroscopy III
MO 13.1–13.31	Tue	16:30–19:00	Poster.IV	Poster 1: Cold Molecules, Femtosecond Spectroscopy, Molecular Dynamics
MO 14.1–14.30	Wed	16:30–19:00	Poster.IV	Poster 2: Biomolecules, Electronic Spectroscopy, Experimental Techniques, Quantum Chemistry, Various Topics
MO 15.1–15.10	Thu	10:30–13:00	V7.03	SYRA: Ultracold Rydberg Atoms and Molecules 3
MO 16.1–16.8	Thu	10:30–12:30	V38.02	Collisions and Spectroscopy in He-Droplets
MO 17.1–17.8	Thu	10:30–12:45	V38.03	Femtosecond Spectroscopy IV
MO 18.1–18.7	Thu	14:00–16:00	V38.02	Molecular Dynamics
MO 19.1–19.7	Thu	14:00–16:00	V38.03	Cold Molecules II
MO 20.1–20.6	Thu	14:00–16:00	V57.05	Atomic clusters (with A)
MO 21.1–21.30	Thu	16:30–19:00	Poster.IV	Poster 3: Cluster, Collisions, Energy Transfer, Photochemistry, Spectroscopy in He-Droplets
MO 22.1–22.6	Fri	10:30–12:00	V38.02	Cluster
MO 23.1–23.5	Fri	10:30–12:00	V38.03	Cold Molecules III

Mitgliederversammlung Fachverband Molekülphysik

Dienstag 12:30–13:00 Raum V38.03

- Bericht
- Symposien, Struktur der Tagung
- Verschiedenes

MO 1: Vibrational Spectroscopy

Time: Monday 10:30–12:45

Location: V38.03

Invited Talk

MO 1.1 Mon 10:30 V38.03

Vibrational Molecular Interferometry — ●HERMAN L OFFERHAUS¹, ERIK T GARBACK¹, SHAUL MUKAMEL², ALEXANDER CW VAN RHIJN¹, CEES OTTO³, and JENNIFER L HEREK¹ — ¹Optical Sciences group, University of Twente, the Netherlands — ²Department of Chemistry, University of California, Irvine, USA — ³Medical Cell BioPhysics group, University of Twente,

We demonstrate an implementation of a CARS microscopy method that is based on an interaction picture centered on the molecules, as proposed in [1], rather than the interacting fields. It provides an intuitive and unified description of the various signal contributions, allowing easy extraction of the vibrational response. Three optical fields create a pair of Stokes Raman pathways that interfere in a single vibrational state. Frequency modulating two of the fields leads to amplitude modulations of the signals, which we refer to as vibrational molecular interferometry (VMI). The modulation depth that we observe is comparable to that found in SRS, and allows imaging at high speed free of the non-resonant background that plagues coherent anti-Stokes Raman scattering (CARS) measurements. The demonstration is on a narrowband system and does not offer a large improvement in practical terms over existing SRS strategies, except that it can distinguish between electronic and vibrational transitions and avoids signals from Kerr-lensing. The new strategy is not limited to narrowband CARS and broadband extensions are possible. [1] Rahav, S. & Mukamel, PNAS 107, 4825-4829,(2010).

MO 1.2 Mon 11:00 V38.03

The full characterization of the third-order nonlinear susceptibility using single-beam-CARS — ●ALEXANDER WIPFLER, JEAN REHBINDER, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Single-beam-CARS setups circumvent the experimental challenge of superposing two laser pulses in space and time. However the information on the nonlinear susceptibility is often poor compared to conventional CARS and spontaneous Raman measurements. We present a method that allows for the full characterization of the susceptibility by introducing a phase gate in the excitation spectrum. The phase of this gate is subsequently set to four different values which makes a double quadrature spectral interferometry (DQSI) operation possible. This operation delivers amplitude and phase of the third-order nonlinear susceptibility. The theoretical background including simulations of the scheme and experimental results on toluene will be presented. As amplitude and phase are obtained, the information on the susceptibility gained with our method exceeds the one from conventional CARS experiments and even spontaneous Raman measurements.

MO 1.3 Mon 11:15 V38.03

Multimodal non-linear imaging with shaped femtosecond pulses — ●JEAN REHBINDER, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Multimodal non-linear imaging takes advantage of the simultaneous generation of different optical signals, like second and third harmonic generation (SHG and THG), two-photon excited fluorescence (2PEF) and four-wave mixing (FWM). SHG and THG highlight structured molecules and interfaces, whereas 2PEF is generated by specific fluorophores. FWM, on the other hand, provides contrast based on the specific third-order nonlinear susceptibility. A promising way to improve multimodal non-linear imaging is phase and amplitude shaping of the excitation pulses. Contrast and selectivity can be improved by addressing specific fluorophores emitting in the same spectral region or even by retrieving the Raman information. This work in based on the phase and amplitude shaping of a single beam from a broadband Ti:Sapphire oscillator applied to microspectroscopy. A first benchmark is presented by comparing the effect of standard Taylor-phase distortions on the different non-linear signals. The separation of spectrally overlapping 2PEF and FWM signal is studied in a plant cell. We also discuss the effect of optimization of SHG or FWM using imaging of a tendon from a rat-tail.

MO 1.4 Mon 11:30 V38.03

Quantitative data analysis in hyperspectral CARS imaging — ●GREGOR HEHL¹, ALEXANDER KOVALEV², and ANDREAS VOLKMER¹ — ¹3. Physikalisches Institut, Universität Stuttgart — ²Department of Zoology, Christian-Albrechts-Universität Kiel

Hyperspectral coherent anti-Stokes Raman scattering (CARS) imaging, the combination of spectrally and spatially resolved CARS detection, offers access to the full wealth of chemical and physical structure information encoded in vibrational signatures of chemical species on the sub-micron length-scale. Because of the coherent nature of the CARS process, a complex spectrum of the third-order nonlinear susceptibility is probed. However, the actual measurement of the CARS spectrum yields its power spectrum. In order to reconstruct the linear Raman response of the sample a spectral phase retrieval is necessary. Two different methods for the qualitative phase-retrieval have been proposed, that is the maximum entropy method (MEM) and the Kramers-Kronig transform. In this work, we demonstrate the full quantitative reconstruction of Raman responses of skin model lipids based on MEM. We show that identical information is obtained from CARS and spontaneous Raman spectra provided that the full coherent nature of the CARS experiment is taken into account. The proposed analysis scheme for hyperspectral CARS data allows fast chemical imaging of living cells and tissues in a label-free and fully quantitative manner.

MO 1.5 Mon 11:45 V38.03

Coherent Anti-Stokes Raman Scattering (CARS) with tunable broadband excitation and narrowband probe pulse — ●MATTHIAS LÜTGENS, SUSANA CHATZIPAPODOPOULOS, and STEFAN LOCHBRUNNER — Universität Rostock, Institut für Physik, 18055 Rostock

Coherent anti-Stokes Raman scattering (CARS) spectroscopy is a powerful tool to investigate vibrational modes and their pure dephasing parameters. We present a CARS technique which involves a broadband, coherent excitation of one or several vibrational modes covering a broad range of vibrational frequencies via a femtosecond, broadband Stokes and a narrowband Raman pump beam. The coherent superposition is probed with a narrowband probe beam in the ps range. For this purpose we developed a narrowband ps - non-collinear optical parametric amplifier (NOPA) that allows us to measure CARS time traces with significant higher spectral resolution compared to other fs-CARS setups without losing the ability to monitor dephasing times by the use of time-delayed probe pulses. The capability of the here presented setup is demonstrated by applying this method to different model systems. We show characteristic CARS spectra including numerical simulations of the signal that allows the determination of the energetic position of vibrational modes as well as the dephasing time T_2 .

MO 1.6 Mon 12:00 V38.03

FTIR- and Ramanspectroscopy of Substituted Paracyclophane Molecules — ●JÖRG HERTERICH, SUSANNE ZEISSNER, INGO FISCHER, and THIEMO GERBICH — Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg

The vibrational structures of three paracyclophanes were investigated, ortho-dihydroxy-[2.2]paracyclophane (o-DHPC), monohydroxy[2.2]paracyclophane (MHPC) and 2,11-dithia[3.3]paracyclophane.

Gas-phase infrared spectroscopy helps to identify the most stable isomer in the gas phase, while FT-Raman spectroscopy permits to study the low-frequency vibrations that give insight into the pi-pi-interactions of the molecules. For o-DHPC the IR spectrum confirms that the EZ rotamer dominates, while for MHPC the spectra indicate a larger contribution of the Z rotamer than expected. The Raman spectrum of 2,11-dithia[3.3]paracyclophane showed a dominance of the trans isomer. The Raman spectra also show that the wavenumber of the lowest frequency twist mode is overestimated by density functional theory in all three molecules.

MO 1.7 Mon 12:15 V38.03

IR spectroscopy on liquid hydrogen isotopologues — ●ROBIN GRÖSSLE — KIT (Karlsruhe Institute of Technology), Institute for

Technical Physics - Tritium Laboratory Karlsruhe, Germany

Future fusion facilities like **ITER** and **DEMO** will have huge amounts of tritium and deuterium circulating in their systems as fuel for the fusion plasma. The T_2 inventory of first generation power plants will be about 2 to 3 kg, with a throughput of approx. 1 kg per hour. One important capability of the T_2 cycle is to reprocess unburned fuel and to purge tritium and deuterium. For hydrogen isotopologue processing the **Isotope Separation System (ISS)** is available, applying a cascade of cryogenic distillation columns to enrich the T_2 .

Before reinjecting the tritium back to fusion process, its purity has to be measured without disturbing the distillation process. IR-spectroscopy is being examined as a reliable; reproduceable, fast and non invasive analytic technique for composition analysis of liquid hydrogen mixtures.

There are several major challenges on the way to a reliable IR measurement method: On the one hand the hydrogen sample has to be cooled to temperatures of about 20 Kelvin. And on the other hand the IR source and the detector are at room temperature. So enough cooling power and a sufficient thermal insulation are required. But also the analysis of IR spectra is not straight forward due to the overlap of spectral features from the six ($H_2, HD, D_2, HT, DT, T_2$) hydrogen molecules.

MO 1.8 Mon 12:30 V38.03

Raman Studies of Ionic Liquids with Weakly Coordinating Anions — SUSANA CHATZIPAPOPOULOS¹, ●FRANK FRIEDRISZIK¹, DANIELA KERLÉ², OLIVER KÜHN¹, STEFAN LOCHBRUNNER¹, RALF LUDWIG², MATTHIAS LÜTGENS¹, and CHRISTIAN ROTH² — ¹University of Rostock, Institute of Physics — ²University of Rostock, Institute of Chemistry

The role of hydrogen bonds in ionic liquids (ILs) is subject of intensive current research. Imidazolium-based ILs show clear hints for hydrogen bonds [1]. In addition Lassègues et al. [2] argue that overtones of the aromatic ring chain vibrations interact with C-H groups in the ring in case of weakly coordinating anions and can explain IR and Raman spectra without involving hydrogen bonds. To clarify the interpretation of vibrational spectra in the regions of the C-H stretch modes of the alkyl chain and the imidazolium ring we investigate ILs by linear Raman and IR spectroscopy. Time-resolved measurements characterizing dephasing processes are done by coherent anti-Stokes Raman spectroscopy (CARS). First experimental results will be presented and discussed in the light of molecular dynamics simulations and quantum chemical calculations.

[1] K. Fumino, A. Wulf, R. Ludwig, *Angew. Chem. Int. Ed.* 2008, 47, 8731 - 8734

[2] J.-C. Lassègues, J. Gronding, D. Cavagnat, P. Johansson, *J. Phys. Chem. A* 2009, 113, 6419 - 6421

MO 2: Electronic Spectroscopy

Time: Monday 10:30–12:15

Location: V38.02

MO 2.1 Mon 10:30 V38.02

Photoionisation of the C3H2 isomer Propargylene — ●MICHAEL STEINBAUER¹, MELANIE LANG¹, INGO FISCHER¹, BARBARA K. CUNHA DE MIRANDA², CLAIRE ROMANZIN², and CHRISTIAN ALCARAZ² — ¹Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany — ²Laboratoire de Chimie Physique, Bât 350, UMR 8000 CNRS & Université Paris-Sud 11, F-91405 Orsay, France

Our group examines the structure and dynamic of reactive intermediates like radicals and carbenes in the gas phase. These species play an important role in the formation of soot in combustion processes or in the chemistry of interstellar space.

Synchrotron radiation as a tunable light source along with Threshold Photoelectron Photoion Coincidence (TPEPICO) spectroscopy can be used to determine ionization energies (IE) of such molecules. As example the threshold photoelectron spectrum of the transient species propargylene, one of three C₃H₂ isomers, is presented. The challenge in these experiments is the handling of the precursor, diazopropargylene. This precursor has to be synthesized in advance for every measurement, is explosive and therefore difficult to handle. However we were able to determine the IE of propargylene and of its precursor. Also the dissociative photoionization of the precursor has been evaluated.

In the talk these results will be presented and compared to the other isomers.

MO 2.2 Mon 10:45 V38.02

Investigation of a borylene with synchrotron radiation — ●KATHRIN FISCHER¹, MICHAEL SCHNEIDER¹, ANDRAS BÖDI², BERND PFAFFINGER³, HOLGER BRAUNSCHWEIG³, and INGO FISCHER¹ — ¹Institut für Physikalische Chemie, Universität Würzburg, Würzburg, Deutschland — ²Paul Scherrer Institut, Villigen, Schweiz — ³Institut für Anorganische Chemie, Universität Würzburg, Würzburg, Deutschland

With the help of synchrotron radiation the borylene complex [(OC)₅Cr=B=N(SiMe₃)₂] was ionized and its dissociation studied. The TEPEPICO method was employed and the experiments were carried out at the Swiss Light Source (SLS). The most important dissociation channels were analyzed and the ionization energy (IE) as well as the appearance energies (AE) determined. The CO ligands dissociate sequentially. The dissociation process was quantitatively modeled within the framework of the SSACM and RRKM theory.[1]

[1] B. Sztáray, A. Bodi, T. Bear, *J. Mass. Spectrom.*, 2010, 45, 1233 - 1245.

MO 2.3 Mon 11:00 V38.02

Photoionisation of fluorenyl and diphenylmethyl — ●MELANIE LANG — Institute of Physical and Theoretical Chemistry of Würzburg, Am Hubland, D-97074 Würzburg, Germany

Due to environmental and health issues it is useful to reduce or prevent the formation of soot and polycyclic aromatic hydrocarbons (PAH). Therefore understanding soot and PAH formation is essential. We examined two radicals, fluorenyl (C₁₃H₉Br) and diphenylmethyl (C₁₃H₁₁) which are possible intermediates in hydrocarbon combustion. We used Synchrotron radiation as a tunable light source to carry out Threshold Photoelectron Photoion Coincidence (TPEPICO) Spectroscopy to determine ionization energies (IE) of both radicals. We used 9-bromofluorene (C₁₃H₉Br) as a precursor to create the fluorenyl and benzhydrylamine (C₁₃H₁₁NH₂) as precursor for diphenylmethyl radical by flash pyrolysis. As both are solids at room temperature both precursors had to be heated to be transferred in the gas phase. The resulting threshold photoelectron spectra (TPES) of both radicals are presented. The extracted IE values are compared to previous results of other groups gained by electron impact experiments. For fluorenyl the comparison shows good agreement with the other results. In contrast the IE of diphenylmethyl detected by the TPES differs from the IE obtained by electron impact techniques. Reasons for this observation will be discussed. Since the precursor dissociative photoionization becomes important at moderate excess energies, it might be discussed whether experiments with different precursors should be carried out in addition.

MO 2.4 Mon 11:15 V38.02

Photoionization of hydroxy-substituted [2.2]paracyclophanes with VUV synchrotron radiation — ●PATRICK HEMBERGER¹, CHRISTOF SCHON², ANDRAS BODI¹, MICHAEL STEINBAUER¹, KATHRIN H. FISCHER², and INGO FISCHER² — ¹Paul Scherrer Institute, Molecular Dynamics Group, CH-5232 Villigen PSI — ²Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg

π -conjugated molecules are widely applied in optoelectronic devices such as organic light emitting diodes. Paracyclophanes are possible new candidates to expand the variety of these materials because of their interesting physical properties, like the coupling between the two benzene rings. The photoionization and dissociative photoionization of hydroxy-substituted [2.2]paracyclophanes were investigated at the VUV beamline of the Swiss Light Source, especially the substituent effects on the ionization energies when the benzene frameworks are hydroxy-substituted. At a photon energy of around 10 eV, the sample starts to dissociatively photoionize. The most prominent channel is the dissociation of both C-C bonds of the CH₂-CH₂ bridges in para position between the two phenol rings leading to the molecule fragmenting

in half. The data were subsequently modeled in order to obtain appearance energies, which then lead to bond dissociation energies and other thermochemical data. In addition calculations were performed, which reveal that even DFT functionals, which take into account dispersion interactions (ω -B97XD), fail to predict the appearance energies correctly.

MO 2.5 Mon 11:30 V38.02

Spectroscopic Studies of the Electron Transfer in a Photocatalytic System based on an Ir(III)-Complex — ●ALEXANDRA PAZIDIS¹, ALEKSEJ FRIEDRICH¹, ANTJE NEUBAUER¹, FELIX GÄRTNER², HENRIK JUNGE², MATTHIAS BELLER², and STEFAN LOCHBRUNNER¹ — ¹Institut für physics, University of Rostock, Germany — ²Leibniz Institut für Catalysis Rostock, Germany

Iridium (III)-complexes have recently gained attention as photosensitizers in homogeneous water-reducing systems.

We investigate the excited state dynamics of [Ir(ppy)₂(bpy)]⁺ (Ir-PS) in a photocatalytic system for hydrogen generation. In the primary reaction steps, the Ir(III)-complex is excited by light and relaxes to the lowest excited triplet state. Subsequently, it is reduced by triethylamine (TEA) as sacrificial reductant and transfers an electron to an iron-complex, which finally reduces the water to hydrogen.[1]

Emphasis is paid to monitor the processes on different time scales: The time range from fs to ns is investigated by transient absorption spectroscopy, luminescence measurements with a streak camera are done with ps to ms time resolution and real-time irradiation and absorption measurements are used to follow subsequent chemical reactions up to a duration of some minutes.

Rate constants for the quenching of the Ir-PS by TEA and by the iron-complex are determined and a interpretation of involved species is given.

References [1] F. Gärtner et al., *Angew. Chem.* 121, 10147 (2009).

MO 2.6 Mon 11:45 V38.02

Intrinsic Luminescence of Diamondoids in the Ultra-Violet Spectral Region — ●PHILIPP REISS¹, DAVID WOLTER², TORBJÖRN RANDE², ROBERT RICHTER², PETER SCHREINER³, ARNO EHRESMANN¹, and THOMAS MÖLLER² — ¹Institut für Physik, Universität Kassel, 34132 Kassel — ²Institut für Optik und Atomare Physik, Technische Universität Berlin, 10623 Berlin — ³Institut für Organische Chemie, Justus-Liebig-Universität Giessen, 35392 Giessen

Clusters and nanocrystals with semiconducting properties are of in-

terest for science and industry due to their size-dependent electronic structure. While currently only direct band gap semiconductors like GaAs are used in light-emitting devices, luminescence of Silicon nanostructures has already been discovered in 1990 and drew attention to the light emission of elemental indirect band gap semiconductor nanostructures. Despite the focus on Si, the underlying origins of the luminescence which are still not fully determined are expected to be of a more universal nature.

Dispersed luminescence and total luminescence yields of various types of diamondoids have been recorded after photoexcitation with synchrotron radiation. Both the excitation energies and photoemission spectra are in the ultraviolet spectral range. Strong dependencies of emission and absorption spectra on the size and shape of the diamondoids have been measured.

MO 2.7 Mon 12:00 V38.02

Resonant x-ray emission spectroscopy as a tool to study the Hofmeister series in liquids — ●ZHONG YIN¹, KATHARINA KUBICEK¹, IVAN RAJKOVIC¹, WILSON QUEVEDO¹, BRIAN KENNEDY², KRISTJAN KUNNUS³, SIMON SCHRECK³, FRANZ HENNIES², PHILIPPE WERNET³, ALEXANDER FÖHLISCH^{3,4}, and SIMONE TECHERT¹ — ¹Max-Planck-Institut für biophysikalische Chemie, Am Fassberg 11, 37077 Göttingen, Germany — ²MAX-Lab, Lund University, 22100 Lund, Sweden — ³BESSY, Albert-Einstein-Straße 15, 12489 Berlin, Germany — ⁴Universität Potsdam, Karl-Liebknecht-Straße 24-25, 14476 Potsdam, Germany

Understanding the role of inorganic salts in chemical and biological systems is one of the intriguing objectives in current chemical research. Based on their relative entropies of solvation and on their ability to salt-out proteins or denature proteins ions could be classified to be structure makers or breakers (Hofmeister series). The fundamentals underlying this behavior still "remain[s] unexplained by present theories of physical chemistry". Furthermore, static soft XAS measurements yielded sometimes conflicting results. Recently we performed static x-ray emission spectroscopy (XES) experiments at synchrotrons. The differences in the water oxygen K-edge spectra of liquid water and different aqueous salt solutions were studied, tuning the photon energy, thus addressing core-levels in an element- and site-specific way. Data analysis is currently ongoing and shows already promising, intermediate results which should significantly contribute to our understanding of solution chemistry.

MO 3: Quantum Chemistry

Time: Monday 14:00–16:00

Location: V38.02

Invited Talk

MO 3.1 Mon 14:00 V38.02

Quantum chemical description of photo-induced molecular processes — ●ANDREAS DREUW — Interdisziplinäres Zentrum für wissenschaftliches Rechnen, Universität Heidelberg, Deutschland

The development of quantum chemical methods and their application to photo-induced processes in chemistry, biology and physics is one of the most active research fields of contemporary theoretical chemistry. Here, we review briefly existing theoretical approaches and own developments in this field focussing on time-dependent density functional theory and the algebraic diagrammatic construction (ADC) of the polarisation propagator. It will be shown how quantum chemical calculation can lead to an in depth understanding of electronic spectra. Results for photo-electron spectra of small molecules will be shown and the two-photon absorption spectrum of octatetraene will be analyzed.

MO 3.2 Mon 14:30 V38.02

Static and Frequency Dependent Dipole Polarizabilities from the Ground-State Electron Density — ●VIVEKANAND GOBRE¹, ROBERT DiSTASIO JR.², MATTHIAS SCHEFFLER¹, and ALEXANDRE TKATCHENKO¹ — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²Princeton University, Princeton, NJ, USA

Molecular polarizability is an essential observable, and its accurate determination is important, e.g., for calculation of van der Waals interactions. Accurate polarizability calculations in principle require computationally expensive electronic structure methods with an explicit treatment of many-electron excitations. These methods can only be applied to systems with less than about 100 atoms. How-

ever, one is often faced with the problem of computing polarizabilities for large systems with thousands of atoms. We present a parameter-free computationally efficient approach to calculate accurate static and frequency dependent polarizabilities for molecules and non-metallic solids. Specifically, we link the TS-vdW [1] method, which accurately treats hybridization effects, with the self-consistent screening equation from classical electrodynamics [2]. Using only the electron density and reference data for the free atoms, we obtain an accuracy of about 7% for both static polarizabilities and van der Waals coefficients for a wide variety of systems. We illustrate the interplay of hybridization and long-range electrostatic screening effects for the polarizability of large proteins and condensed-matter systems. [1] A. Tkatchenko and M. Scheffler, *PRL* **102**, 073005 (2009); [2] B. U. Felderhof, *Physica* **76**, 486 (1974).

MO 3.3 Mon 14:45 V38.02

Relativistic time-dependent density functional theory and excited states calculations for the Zn₂ and Cd₂ dimers. — ●OSSAMA KULLIE — CNRS et Université de Strasbourg, Institut de Chimie, Laboratoire de Chimie Quantique, 1 Rue Blaise Pascal, F-67008 STRASBOURG cedex, France. ossama.kullie@unistra.fr

In this work I present a (time-dependent) density functional study of the low-lying excited states as well the ground states of the zinc and cadmium dimers Zn₂ and Cd₂. I analyze the spectrum of the dimers obtained from all electrons calculations which are performed using time-dependent density functional with a relativistic 4-components-, and spin-free-Hamiltonian [1]. I will show results for different well-known density functional approximations, in comparing with literature

and experimental values, the results are very encouraging, especially for the lowest excited states of these dimers. However, the results show that only the long-range corrected functionals such CAMB3LYP gives the correct asymptotic behavior for the higher states, for which the best result is obtained, and a comparable result is obtained from PBE0 functional. An outlook for Hg₂ and possibly Cn₂ dimers will be given. [1] O. Kullie, to be published in JPB (2012).

MO 3.4 Mon 15:00 V38.02

Auger spectrum of a water molecule after single and double core ionization — ●LUDGER INHESTER, CARL F. BURMEISTER, GERIT GROENHOF, and HELMUT GRUBMÜLLER — Max Planck Institut für biophysikalische Chemie, Göttingen

The high intensity of Free Electron Lasers (FEL) opens up the possibility to do single-shot molecule scattering experiments. However, even for small molecules radiation damage induced by absorption of high intense x-ray sources is not yet fully understood. To provide insight into this process, we have studied the dynamics of a water molecule in single and double core ionized states by means of electronic transition rate calculations and ab initio molecular dynamics (MD) simulations. From MD trajectories photoionization and Auger transition rates were computed based on electronic continuum wavefunctions obtained by explicit integration of the coupled radial Schrödinger equations. To account for the nuclear dynamics during the core hole lifetime the calculated electron emission spectra for different molecular geometries were accumulated according to time-dependent populations.

We find that, in contrast to the single core ionized water molecule, the nuclear dynamics for the double core ionized water molecule during the core hole lifetime strongly affects the resulting electron emission spectra. In addition, the lifetime of the double core ionized water was found to be significantly shorter than half of the single core hole lifetime.

MO 3.5 Mon 15:15 V38.02

Theoretical investigation of the X-ray adsorption spectra (XAS) of charged chromium-gold clusters using DFT. — ●ROLF WÜRDEMANN, KLAUS ZIMMERMANN, and MICHAEL WALTER — Freiburger Materialforschungszentrum, Freiburg, Germany

Current research using X-ray adsorption spectroscopy (XAS) exhibits a interesting behaviour of the Au_2Cr^+ molecule. While one would expect, that the XAS-spectrum of the charged Au_2Cr^+ dimer differs from the XAS-spectrum of the neutral chromium atom, the spectra are nearly identical. This effect is also known from the charged chromium dimer, where the spectra of the charged dimer and the neutral atom where nearly identical.

Keeping this in mind, we discuss the magnetic ordering, potential

energy surface (PES), binding energies and -distances of the charged Au_2Cr^+ molecule using DFT and compare this with other small Au_nCr^+ molecules ($n < 5$) and the charged chromium dimer.

MO 3.6 Mon 15:30 V38.02

Theoretical study of Ir(III) based systems for photocatalytic water splitting — ●SERGEY BOKAREV, OLGA BOKAREVA, and OLIVER KÜHN — Institut für Physik, Universität Rostock, Rostock, Deutschland

Photocatalytic water splitting into hydrogen and oxygen is a very attractive direction in the search for new energy sources. One of the schemes for a homogeneous water splitting solar cell involves an Ir(III) containing photo-sensitizer, a Fe(II) catalyst, and the sacrificial reductant [1]. In the present work, we focused on the first stage of the process involving the structure of the ground and lowest excited electronic states of $[Ir(ppy)_2(bpy)]^+$ and a number of derivatives in oxidized and reduced forms and their interaction with a sacrificial reductant. Based on the results of TDDFT (LC-BLYP) and CASSCF calculations we assigned the bands in the UV-Vis absorption spectrum and proposed a scheme for the photophysical and photochemical processes involving the lowest excited states of Ir(III) photosensitizers. 1. F. Gärtner et al. Angew. Chem. Int. Ed. 2009, V. 48, P. 9962.

MO 3.7 Mon 15:45 V38.02

DFT Study of Charged Gold Clusters in Different Environments — ●ALEXANDER HELD and MICHAEL WALTER — FMF Uni Freiburg, Germany

The charge dependent cluster capacitance $C(z)$ of gold nanoparticles is investigated in different environments using density functional theory (DFT) calculations.

In the gas phase, $C(z)$ is influenced primarily by electronic shell closing effects and the spatial extent of the excess charge. For gold nanoparticles prepared in a wet chemical process, the ligands may affect the cluster capacitance in different ways. Recent experimental results show evidence for quantized charging effects of quasi-unprotected gold nanoparticles in the ionic liquid $[C_4mim][BF_4]$ for the first time. A peak like shape of $C(z)$ has been observed. This feature is reproduced by our DFT model calculations and is found to originate from a polarity inversion of the ionic liquid surrounding the nanoparticles [1].

Furthermore, the DFT results are interpreted with an electrostatic model. Within the parameters of this model, different shapes of $C(z)$ occur, suggesting further experimental investigations and comparison to other theoretical approaches.

[1] S. F. L. Mertens, C. Vollmer, A. Held, M. H. Aguirre, M. Walter, C. Janiak and T. Wandlowski, Angew. Chem. Int. Ed. 2011, 41, 9735 – 9738

MO 4: Cold Molecules I

Time: Monday 14:00–16:00

Location: V38.03

MO 4.1 Mon 14:00 V38.03

Statistical multichannel quantum defect theory for resonant scattering of ultracold atoms and molecules — ●MICHAEL MAYLE, BRANDON P. RUZIC, and JOHN L. BOHN — JILA, University of Colorado and NIST, Boulder, Colorado, USA

With the advent of state-resolved, ultracold samples of ground state molecules, novel opportunities arise to explore the physics of cold and ultracold molecular collisions. We revisit ultracold atom-molecule scattering by employing a multichannel quantum defect theory treatment that makes a clean distinction between the physics of the complex, which is pertinent when the colliding species are close together, and the physics of the long-range scattering, which is sensitive to such things as the hyperfine states of the atoms and molecule, the low collision energy, and any applied electromagnetic fields. This allows us to describe long-range interactions by means of a few quantum defect parameters while for the short-range part we apply the methods of random matrix theory. Uniting these two techniques, we can assess the influence of highly-resonant scattering in the threshold regime, and in particular its dependence on the hyperfine state selected for the collision.

MO 4.2 Mon 14:15 V38.03

Low energy rare gas - alkali scattering experiments — ●MATTHIAS STREBEL, BERNHARD RUFF, MARCEL MUDRICH, and

FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg

In order to investigate reactive and non reactive collisions between atoms and molecules at very low scattering energies, a magneto-optical trap (MOT) for ultracold ^7Li atoms is combined with a rotating nozzle setup for producing slow beams of cold molecules. Studying reactive scattering processes with collision energies down to 1 meV, we expect to get insight into the quantum mechanical nature of cold reactions.

First measurements of differential and integrated cross sections of elastic collisions with rare gases already show interesting features like rainbow scattering or glory undulations. The suitability of a MOT as a scattering target for low-energy collision experiments with regard to the particular kinematics resulting from a resting target and diagnostics such as fluorescence imaging as a measure for integral cross sections is discussed.

MO 4.3 Mon 14:30 V38.03

Long-range interactions in cold atomic and molecular samples — MAXENCE LEPELERS¹, ROMAIN VEXIAU¹, MIREILLE AYMAR¹, BÉATRICE BUSSEY-HONVAULT², JEAN-FRANÇOIS WYART¹, NADIA BOULOUEFA¹, and ●OLIVIER DULIEU¹ — ¹laboratoire Aimé Cotton, CNRS, Université Paris-Sud, Orsay, France — ²Laboratoire Interdisciplinaire Carnot de Bourgogne, Université de Bourgogne, Dijon, France

Long-range interactions play a crucial role in cold and ultracold physics and chemistry, for example on elastic, inelastic and reactive collisions between atoms and molecules. In this work, we have characterized the long-range interactions for a wide variety of systems being of strong experimental interest. We have calculated the asymptotic electrostatic interaction energy between alkali-metal atoms and diatomic molecules, between erbium atoms, and between oxygen atoms and molecules. In particular, we have focused our study on the Van der Waals contribution which requires a detailed knowledge of the energy spectrum of the two interacting partners. Improved values of dynamic polarizabilities based on accurate *ab initio* calculations as well as on up-to-date spectroscopic analysis have been determined.

We have obtained a huge dispersion in the Van der Waals coefficients, ranging from a few tens of atomic units for $O+O_2$, to a few 10^5 atomic units for polar diatomic molecules in their ground rovibrational level. In the atom-diatom case, we have shown that for sufficiently small distances the rotational levels of the diatomic molecule can be coupled due to the presence of the partner, leading to a complex pattern of potential energy curves, and possibly a complex collisional dynamics.

MO 4.4 Mon 14:45 V38.03

The excited level of the $2p\sigma_u$ electronic state in H_2^+ — ●TIM-OLIVER MÜLLER and HARALD FRIEDRICH — Technische Universität München

In Ref. [1] a new weakly bound vibrational level of the H_2^+ molecular ion with a binding energy of only 1.0851×10^{-9} a.u. ≈ 30 neV is predicted from three-body calculations. It is the (rotationless) excited vibrational level $v = 1$ of the $2p\sigma_u$ electronic state.

It is argued in [1] that calculations using the asymptotic expansion of the effective two-body potential for the ungerade state given by Landau [2] can reproduce neither the bound state energy of the $v = 1$ state nor the scattering properties with sufficient accuracy.

We point out that the $v = 1$ vibrational state can well be described as a bound state in the distant well of the enhanced p-H two-body potential [3] with a binding energy of 0.9749×10^{-9} a.u., very close to the exact result ($\approx 10\%$). The exact scattering properties including the scattering length are also reproduced with good accuracy.

[1] Carbonell J., *et al.*, *Europhys. Lett.* **64**, 316, (2003)

[2] Landau L. D., and Lifschitz E. M., *Theoretische Physik 3, Quantenmechanik* (Akademie-Verlag, Berlin) 1965, p.305.

[3] Damburg R. J., and Propin R. Kh., *J. Phys. B* **1** 681 (1968).

MO 4.5 Mon 15:00 V38.03

Two-Photon-Spectroscopy of YbRb-Towards paramagnetic molecules — FRANK MÜNCHOW, ●CRISTIAN BRUNI, MAXIMILIAN MADALINSKI, and AXEL GÖRLITZ — Institut für Experimentalphysik, HHU Düsseldorf, 40225 Düsseldorf

Ultracold heteronuclear molecules offer fascinating perspectives ranging from ultracold chemistry to novel interactions in quantum gases. Here we report on the spectroscopic investigation of vibrational levels in the electronic ground state of the heteronuclear molecule $^{176}\text{Yb}^{87}\text{Rb}$. Using two-photon photoassociation spectroscopy in a laser-cooled mixture of ^{176}Yb and ^{87}Rb we are able to determine the binding energies of weakly-bound vibrational levels. By means of Autler-Townes spectroscopy we obtain transition rates between vibrational levels of different molecular states. This knowledge is a crucial step towards the realization of YbRb ground state molecules.

MO 4.6 Mon 15:15 V38.03

Kalte Reaktionen von Kohlenwasserstoff-Ketten mit H_2 — ●ERIC ENDRES, THORSTEN BEST and ROLAND WESTER — Institut f. Ionenphysik und Angewandte Physik A-6020 Innsbruck

Die Entdeckung der ersten molekularen Anionen hat eine intensive Suche nach weiteren Anionen in verschiedenen astronomischen Objekten ausgelöst. Als erstes wurde C_6H^- im Labor und in dichten molekularen Wolken identifiziert [1]. Eine genaue Analyse dieses Moleküls ist somit von wesentlicher Bedeutung.

Experimente zum Photodetachment [2] und zu Reaktionen bei

Raumtemperatur mit den atomaren Partnern H, N bzw. O [3] wurden bereits durchgeführt. Bei der Reaktion von negativ geladenen Kohlenwasserstoff-Ketten mit molekularem Wasserstoff liegen noch keine Resultate vor. Jedoch gibt es Hinweise, dass diese eher langsam ablaufen ($k < 10^{-13} \text{cm}^3 \text{s}^{-1}$) [3]. Wegen der Häufigkeit von H_2 im interstellaren Medium ist die genaue Kenntnis der Reaktionsrate der Reaktion dennoch bedeutsam.

Eine kryogene 22-Polige Radiofrequenz-Ionenfalle ermöglicht uns bei langen Speicherzeiten auch die Beobachtung selten ablaufender Reaktionen. Darüber hinaus ist die Temperatur der Falle zwischen 8K und 300K einstellbar, so dass eine mögliche Temperaturabhängigkeit der Reaktion, unter astrophysikalischen Bedingungen, gemessen werden kann [4]. Der aktuelle Stand der Messung wird berichtet.

[1] McCarthy et al. *Ap.J.* 652:L141 (2006); [2] Best et al. *Ap.J.* 742:63 (2011); [3] Eichelberger et al. *Ap.J.* 667:1283 (2007); [4] Otto et al. *Phys. Rev.Lett.* 101:063201 (2008)

MO 4.7 Mon 15:30 V38.03

Position oscillations in ordinary space probed by asymmetries in doppler shifted Auger-ion coincidence spectra — ●TORALF LISCHKE¹, GREGOR HARTMANN¹, ANDRE MEISSNER¹, RAINER HENTGES¹, BURKHARD LANGER², UWE BECKER^{1,3}, and OMAR AL-DOSSARY³ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Freie Universität Berlin, Berlin, Germany — ³King Saud University, Rhiyad, Saudi Arabia

Inversion symmetry erases the distinction between left and right positions in ordinary space. Instead, coherent superpositions of both sites *gerade* and *ungerade* states are built, which are energetically non-degenerate. Superimposing these superpositions should give rise to reestablishment of the original position states which should, however, oscillate with a frequency proportional to the energy difference between the original *gerade* and *ungerade* states. We show indirect evidence for this behavior in ordinary space analogous to the already observed behavior in flavor space. This behavior was an oscillation between the two strangeness components K and \bar{K} over time. We observe such an oscillation in ordinary space in an indirect way by probing the asymmetry between so called right and wrong Doppler shifted components of resonant Auger electrons following K-shell photo excitation of O_2 . By selecting two types of resonant Auger transition with severely different Auger lifetimes we could make predictions on the expected asymmetry. The asymmetry values of approximately 0.3 and 0.0 for the two cases predicted by our model could be unexpectedly well verified.

MO 4.8 Mon 15:45 V38.03

The effect of orientation in molecular double-slit experiments — ●GREGOR HARTMANN¹, MARKUS BRAUNE², ANDRE MEISSNER¹, TORALF LISCHKE¹, and UWE BECKER¹ — ¹Fritz-Haber-Institut der Max-Planck Gesellschaft, Faradayweg 4-6, 14195, Germany — ²DESY, Notkestr. 85, 22607 Hamburg, Germany

Molecular double-slit experiments are a subject of high actual interest for the study of entanglement in ordinary space. The interference pattern observed on a screen in regular macroscopic double-slit experiments are exhibited as oscillations of the partial photoionization cross section of homonuclear diatomic molecules, the prototype of a molecular double-slit experiment. These oscillations were predicted already more than 40 years ago by Cohen and Fano and were experimentally verified by many groups since then. However, Cohen and Fano prediction was for randomly oriented molecules integrating over all possible directions of the molecular axis. Nowadays it is also possible to measure the photoionization properties of oriented molecules. The most fundamental system for such studies is molecular hydrogen. Here we present measurements of the same interference properties but performed on an oriented sample of H_2 molecules. The experimental data cover an energy range from 20 to 500 eV electron kinetic energy. The results show a clear phase shift of $\pi/2$ with respect to the random sample due to the differentiation of the integral axis orientation sample transforming a sin curve into a cos curve. This differentiation effect could be unambiguously proved for the first time.

MO 5: Experimental Techniques

Time: Monday 16:30–19:00

Location: V38.02

MO 5.1 Mon 16:30 V38.02

High Energy Velocity Map Imaging for Experiments at FEL — ●AXEL HUNDERTMARK^{1,2}, ARNAUD ROUZÉE^{1,2}, PER JOHNSON³, and MARC J. J. VRAKKING^{1,2} — ¹Max-Born-Institut, Max-Born Straße 2A, D-12489 Berlin, Germany — ²FOM Institute AMOLF, NL-1098 XG Amsterdam, Netherlands — ³Department of Physics, Lund University, Post Office Box 118, SE-22100 Lund, Sweden

Free Electron Lasers (FEL) offers high photon flux in the VUV/X-ray regime with fs pulse duration. Such conditions give the opportunity to study multi-photon multiple ionization of atoms or molecules in this photon range and in combination with a time delayed laser allow to carry out pump-probe experiments. We present preliminary results obtained at the Linac Coherent Light Source (LCLS) and Free-electron Laser in Hamburg (FLASH) on the multi-photon ionization of rare gas atoms, the ionization dynamics of Br₂ molecule and on the molecular alignment of CO₂ molecules induced by a first laser excitation. The measurements were done with a newly developed high energy Velocity Map Imaging spectrometer (VMIs) which records the photoelectron angular distribution over an energy range that can extend to 1.5 keV.

MO 5.2 Mon 16:45 V38.02

Characterisation of a high resolution spatial map ion imaging setup — JOHANNES VON VANGEROW¹, ●MARTIN STEI¹, ADITYA KELKAR¹, RICO OTTO^{1,2}, THORSTEN BEST¹, and ROLAND WESTER¹ — ¹Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck — ²now at: Department of Chemistry, University of California, San Diego

Over the past decade velocity map imaging (VMI) [1] has emerged as a well established and widely used technique for studying molecular reaction dynamics. The electrostatic lens arrangement of a VMI spectrometer also provides the flexibility to operate in spatial map imaging (SMI) mode. In recent years efforts have been directed towards applying the SMI technique for imaging biological tissue as well as for beam profiling of neutral, ion and laser beams [2,3]. However, a detailed characterisation in terms of resolution and imaging properties is still missing. Here we report the characterisation of the spatial map imaging mode of our 3D VMI spectrometer using multi-photon ionisation of toluene in a focused laser beam. A spatial resolution better than 5 μm and a 3 dimensional SMI mode will be demonstrated and compared with simulations.

- [1] A. T. Eppink, D. H. Parker, Rev. Sci. Instrum. 68, 3477 (1997)
- [2] M. Brouard, A.J. Johnsen, A. Nomerotski, C.S. Slater, C. Valance, and W.H. Yuen, JINST 6, C01044, (2011)
- [3] M. Schultze, B. Bergues, H. Schröder, F. Krausz and K. L. Kompa, New J. Phys. 13, (2011)

MO 5.3 Mon 17:00 V38.02

Instrumentierung und Messungen von Photoelektron-Photoionkoinzidenzspektren — ●SASCHA DEINERT, LEIF GLASER, MARKUS ILCHEN, FRANK SCHOLZ, JÖRN SELTMANN, PETER WALTER und JENS VIEFHAUS — Deutsches Elektronen Synchrotron, Notkestraße 85, 22609 Hamburg

Zur effizienten Messzeitnutzung an Synchrotronstrahlungsquellen wurde ein Spektrometer für Photoelektron-Photoionkoinzidenzen entwickelt. Mit Simulationen (Simion, Mathematica) wurde das konventionelle Konzept (z.B. [1]) optimiert, das ein kurzes Flugzeitspektrometer für den effizienten Ionennachweis [2] kombiniert mit einem Flugzeitspektrometer, welches mittels magnetischer Flasche die in den gesamten Raumwinkel emittierten Photoelektronen nachweisen kann [3].

Nach einer instrumentellen Beschreibung werden Messungen zur atomaren und molekularen Photoionisation vorgestellt, die an der BW3-Beamline bei DORIS/DESY in Hamburg vorgenommen wurden und das Potential der Spektrometerkombination für geplante Messungen am P04-Strahlrohr bei PETRA III aufzeigen.

- [1] P. Kruit, F.H. Read, J. Phys. E 16 (1983) 313
- [2] C. Wiley, I.H. McLaren, Rev. Sci. Instrum. 26 (1955) 1150
- [3] H.D. Eland, R. Feifel, Chemical Physics 327 (2006) 85*90

MO 5.4 Mon 17:15 V38.02

Design of a new pixel type position sensitive anode for ion and electron spectroscopy — ●ANDRE MEISSNER¹, GREGOR HARTMANN¹, TORALF LISCHKE¹, UWE BECKER^{1,3}, BURKHARD

LANGER², and OMAR AL-DOSSARY³ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Freie Universität Berlin, Berlin, Germany — ³King Saud University, Riyadh, Saudi Arabia

Position sensitive anodes are the key element for all photoionization and particle impact ionization experiments which provide full information on the momentum distribution of the fragmenting system, either ions or electrons. Famous examples for such experiments are the measurements performed by the COLTRIMS method. Similar systems have been developed also by other groups. One of the key problem in these experiments, particularly for larger target systems is the so called multi-hit capability. Delay line anodes and pixel based anodes show a capacity in this sense of 10 to 20. In order to improve this capacity we have developed a system for the pixel type arrangement. This should allow us to increase the multi-hit capability up to 100. In this case it could be used for many fragmentation events of larger molecules but also for multi electron emission events being probed in coincidence. The basic design of this type of anode will be presented and its possible applications are discussed.

MO 5.5 Mon 17:30 V38.02

Accurate depolarization measurements of all six hydrogen isotopologues — ●MAGNUS SCHLÖSSER¹, TIM M. JAMES², SEBASTIAN FISCHER¹, RICHARD J. LEWIS³, HELMUT H. TELLE², and BEATE BORNSCHNEIN¹ — ¹Tritium Laboratory Karlsruhe, Institute for Technical Physics, Karlsruhe Institute of Technology, GER — ²Department of Physics, Swansea University, UK — ³Instituto Pluridisciplinar, Universidad Complutense de Madrid, ES

The calibration of the Laser Raman system (LARA) of the Karlsruhe TRITium Neutrino experiment (KATRIN) is required for the accurate accountability of the tritium gas in the source tube. In the current approach for the quantitative analysis of the LARA system, the experimentally measured spectrum will be compared to a theoretically calculated spectrum. The intensities of the theoretical spectra can be calculated from quantum mechanical matrix elements. However, these theoretical matrix elements, which can be found in literature, need experimental verification before they can be employed for the LARA analysis.

One elegant way to verify these matrix elements are the so-called depolarization measurements. In this presentation we show a novel methodology for these measurements and their analysis. This takes into account laser-polarisation related effects in optical components and considers the experimental geometry. Finally, the resulting depolarisation ratios of all hydrogen isotopologues (T₂, DT, D₂, HT, HD, H₂) are presented.

MO 5.6 Mon 17:45 V38.02

Identification and Non-destructive State Detection of Molecular Ions — KEVIN SHERIDAN, AMY GARDNER, NIC SEYMOUR-SMITH, and ●MATTHIAS KELLER — University of Sussex, UK

Cold molecules have a multitude of applications ranging from high resolution spectroscopy and tests of fundamental theories to cold chemistry and, potentially, quantum information processing. Prerequisite for these applications is the cooling of the molecules' motion and its non-invasive identification. Furthermore, the internal state of the molecules needs to be prepared and non-destructively detected. The cooling of the motion and trapping of molecular ions can be accomplished by trapping them in an rf-trap alongside laser cooled atomic ions. We have developed a novel technique to measure the average charge to mass ratio of trapped ions with high precision by broadband excitation of the ions' COM-mode motion and measuring their laser induced fluorescence. The FFT of the fluorescence's autocorrelation provides the COM-mode spectrum with a good SNR for measurement times as low as 100ms and kinetic energy injections of less than a few mK. The method is limited only by the required interrogation time and the motional coupling of the constituents of the mixed ion crystal. Employing state selective laser induced dipole forces we aim to detect the internal state of molecular ions by mapping the state information onto the ions' motion. The scheme promises mitigation of the effect of laser polarisation and the distribution of population across Zeeman sublevels and it may be applicable for a larger number of simultaneously trapped molecules.

MO 5.7 Mon 18:00 V38.02

A High Resolution Ion Mobility Spectrometer to preselect molecular conformers for gas-phase spectroscopy — ●STEPHAN WARNEKE, KEVIN PAGEL, GERARD MEIJER, and GERT VON HELDEN — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

A key technique to investigate biomolecules in the gas phase is mass spectrometry and many methods are available to obtain mass/charge ratios with very high accuracy. However, with MS methods only little information on the higher order structure is obtained - even though their knowledge is crucial for the understanding of intra- and intermolecular interactions as well as the function of the molecule. Two techniques that are sensitive to the higher order structure of gas-phase molecules are ion mobility spectrometry (IMS) and infrared (IR) spectroscopy, of which both can be combined with mass spectrometry.

In IMS, the absolute (angle averaged) collision cross section and, thus, the effective size of the ion is determined. Additionally, when ions coexist in different conformations, they can be separated in space and time to allow for experiments on both mass/charge as well as (geometrical) shape/charge selected ions.

In this talk, the setup of our high resolution ion mobility spectrometer and first results on peptides and small proteins will be presented. In addition, strategies to utilize the existing instrument as a tool to conformationally pre-select biomolecules for gas-phase IR spectroscopy experiments will be discussed.

MO 5.8 Mon 18:15 V38.02

Broadband Microwave Spectroscopy of Large Molecules — ●DAVID SCHMITZ, VIRGIL ALVIN SHUBERT, THOMAS BETZ, and MELANIE SCHNELL — Max-Planck Advanced Study Group at the Center for Free-Electron Laser Science, Hamburg, and Max-Planck-Institut für Kernphysik, Heidelberg

Isomerization reactions are a fundamental class of chemical transformations and their understanding is essential for the detailed description of chemical reactions in general. Before the dynamics of isomerization reactions between the different structural isomers, i.e., conformers, can be understood, they themselves have to be identified and characterized. For this, we have constructed a novel broadband rotational spectrometer, covering the 2-8 GHz range within a single acquisition. The obtained spectra, aided by theory, allow us to investigate the conformational structures and preferences of large molecules, e.g. crown ethers and their complexes with water or metals. Furthermore, we can gain insight about isomerization dynamics by pumping the molecules above isomerization barriers using a tunable infrared laser and then to probe using a chirped microwave pulse¹. Here, we will present this technique and report initial results on the rotational spectrum of 15-crown-5 ether.

¹Dian et al., *Science*, **320**, (2008), pp. 924-928

MO 5.9 Mon 18:30 V38.02

Nitrogen inversion tunneling in the microwave spectrum of diethyl amine and methyl tert-butyl amine — ●HA VINH LAM

NGUYEN and WOLFGANG STAHL — Institute of Physical Chemistry, RWTH Aachen University, Germany

Proton tunneling is an important class of large amplitude motions, which appears in some secondary amines like dimethyl amine (DMA) and ethyl methyl amine (EMA). This causes splittings of the rotational lines of 2646.0 MHz and 1981.0 MHz for DMA and EMA, respectively.

In the case of diethyl amine, CH₃CH₂NHCH₂CH₃, we found a barrier to inversion of 18.31 kJ/mol from the separation between the lowest symmetric and antisymmetric inversion energy level of E = 760.77062(20) MHz for all *c* type transitions. *b* type lines show only narrow splittings due to Coriolis coupling. Moreover, due to the nuclear spin of I = 1 of the ¹⁴N nucleus hyperfine splittings arise. The inversion splittings of diethyl amine were described with molecular parameters using the programs *spfit* and *spcat* by Pickett instead of reporting the splitting of each single rotational transition as in previous work.

Methyl tert-butyl amine, (CH₃)₃CNHCH₃, is a further secondary amine we investigated. Quantum chemical studies showed that the most stable conformer has a C_S symmetry and proton tunneling is possible. A preliminary assignment with Pickett's *spfit* code including overall rotational and tunneling effects was carried out. The separation between the two inversion energy levels is 698.903(99) MHz for *c* type lines in this case. Centrifugal distortion and ¹⁴N hyperfine coupling effects have not yet been considered.

MO 5.10 Mon 18:45 V38.02

Rovibrational eigenenergy structure of the [H,C,N] molecular system — ●GEORG CH. MELLAU — Physikalisch-Chemisches Institut, Justus-Liebig-Universität, 35392 Giessen, Germany

The HCN and HNC linear molecules provide an important and well-studied prototype system of an isomerizing molecule, they are one of the few chemically bound isomers accessible to a full and accurate ab initio study of their electronic potential energy surface and their nuclear motion states [1]. Using Hot GAs Molecular Emission (HOTGAME) spectroscopy the complete experimental list of the first 5000 rovibrational eigenenergies has been established for this system [2,3] obtaining the first complete frequency domain description of a polyatomic molecule up to high rovibrational excitations. Especially interesting are the delocalized states of the [H,C,N] molecular system which cross the barrier and therefore cannot be uniquely associated with a particular isomer. The rovibrational structure of these states is one of the key features needed for a quantum mechanical understanding of the HCN-HNC model reaction. To support HOTGAME experiments covering such high molecular excitations [4] the rovibrational eigenenergy structure of the isomerization states have been studied by labeling the complete set of calculated ab-initio eigenenergies [5] with vibrational quantum numbers [6]. [1] T. Mourik et al., *J.Chem.Phys.* 115, 3706 (2001). [2] G. Mellau, *J.Chem.Phys.* 133,164303 (2010). [3] G. Mellau, *J.Chem.Phys.* 134,234303 (2011). [4] G. Mellau, *J.Mol.Spectrosc.* 269, 12 (2011). [5] Harris et al., *MNRAS* 367, 400 (2006). [6] G. Mellau, *J.Chem.Phys.* 134,194302 (2011).

MO 6: Femtosecond Spectroscopy I

Time: Monday 16:30–19:00

Location: V38.03

MO 6.1 Mon 16:30 V38.03

CRASY: Correlated Rotational Alignment Spectroscopy with 70 MHz resolution — ●CHRISTIAN SCHRÖTER and THOMAS SCHULTZ — Max-Born-Institut, Berlin

Our aim is the investigation of photochemical reactions in biological chromophores, such as DNA-bases. Biological chromophores can occur in different structural conformations, and the assignment of spectroscopic data to a specific molecular structure is difficult. With CRASY, we are able to measure correlated data to characterize nuclear and electronic structure simultaneously (1). CRASY is a method which combines rotational spectroscopy in the time domain with femtosecond-pump-probe experiments. An IR pulse generates a coherent rotational wave packet by means of non-adiabatic alignment. After a variable delay, we probe the wave packet by a UV pulse which excites and ionizes the molecule via a resonant electronic state. A Fourier transform of collected electron and ion signals reveals the rotational Raman spectrum for each species in the sample. For the reliable assignment of

biomolecular isomers, we require a good rotational resolution. Here we present CRASY measurements with a resolution below 70 MHz, sufficient for the characterization of DNA-base tautomers.

(1) *Science* 333, 1011 (2011)

MO 6.2 Mon 16:45 V38.03

Circular Dichroism in the Photoelectron Angular Distributions of Camphor and Fenchone observed via Multiphoton Ionization — ●CHRISTIAN LUX, TOM BOLZE, CRISTIAN SARPE, MATTHIAS WOLLENHAUPT, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

Photoelectron Circular Dichroism (PECD) [1] was investigated the last decade on small chiral molecules using vacuum ultraviolet (VUV) synchrotron radiation. The observed asymmetries in PECD arise in forward/backward direction with respect to the light propagation and show an effect several orders larger than in conventionally observed CD. Resonance Enhanced Multi-Photon Ionization (REMPI) in mass

spectroscopy of chiral molecules using ultrashort laser pulses [2,3] in the visible and near UV showed also strong asymmetries in the absorption of circularly polarized light.

In this contribution we present that PECD is also accessible using REMPI with UV femtosecond laser pulses [4]. The obtained Photoelectron Angular Distributions in the 2+1 REMPI of Camphor and Fenchone contain highly structured asymmetries up to 20%.

[1] I. Powis in S. A. Rice (Ed.): *Adv. Chem. Phys.* **138**, 267-329 (2008)

[2] C. Logé, A. Bornschlegl, U. Boesl, *Anal. Bioanal. Chem.* **395**, 1631-1639 (2009)

[3] P. Horsch, G. Urbasch, K.-M. Weitzel, *Z. Phys. Chem.* **225**, 587-594 (2011)

[4] C. Lux, M. Wollenhaupt, T. Bolze, Q. Liang, C. Sarpe, T. Baumert (*in preparation*) (2011)

MO 6.3 Mon 17:00 V38.03

Magic-angle and anisotropy calculations for arbitrarily polarized pump-probe spectroscopy — JOHANNES BUBACK, SEBASTIAN SCHOTT, ANDREAS STEINBACHER, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

We calculate anisotropy effects in pump-probe transient-absorption experiments with arbitrarily polarized pump and probe pulses. The versatility of the approach allows us to simulate various experimental scenarios, e.g. with femtosecond laser pulses generated by a polarization pulse shaper, and to derive magic-angle conditions for which the pump-probe signal is independent of the angle between pump and probe transition dipole moments. Whereas this is well-known for studies with linearly polarized pump and probe pulses, we discuss specifically the case of a polarization-shaped pump pulse for quantum control experiments, as well as the case of a circularly polarized probe pulse for transient circular-dichroism measurements.

MO 6.4 Mon 17:15 V38.03

Pump-Probe simulations for single trapped molecular ions — MARKUS KOWALEWSKI¹, STEFFEN KAHRA², GÜNTHER LESCHHORN², TOBIAS SCHAEZT^{2,3}, and REGINA DE VIVIE-RIEDLE¹ — ¹Department Chemie, Ludwigs-Maximilians Universität München — ²Max-Planck-Institut für Quantenoptik, Garching — ³Albert-Ludwigs-Universität, Freiburg

Ion traps offer a great possibility to handle cold single molecular ions without environmental interactions. Ultrashort and intense laser pulses are a well established tool for studying and controlling the molecular dynamics. Both methods are combined in a new experiment with MgH⁺ ions. It is demonstrated, that a pump-probe experiment under these conditions is possible.

In this talk we present the theoretical model which faces the the problems arising in this novel parameter regime. In contrast to femtosecond experiments in the gas or condensed phase the same molecule is excited by the laser several times. Thus they are subject to internal heating, which has to be treated in the theory and handled in the experiment. Moreover an extended pump-probe pulse scheme is developed which keeps the ions cool.

MO 6.5 Mon 17:30 V38.03

Simulation of Vibrational Dephasing of I₂ in a Krypton Matrix — MAX BUCHHOLZ¹, FRANK GROSSMANN¹, and BURKHARD SCHMIDT² — ¹Institut für Theoretische Physik, Technische Universität Dresden, 01062 Dresden — ²Institut für Mathematik, Freie Universität Berlin, Arnimallee 6, 14195 Berlin-Dahlem

In four-wave mixing experiments on iodine in a krypton matrix in the Apkarian group [M. Karavitis et al, *Phys. Chem. Chem. Phys.* **7**, 791 (2005)], the decay of coherences between vibrational eigenstates in the electronic ground state of the iodine molecule has been investigated for a range of eigenstates and temperatures. Motivated by these experiments, we study the dynamics of an I₂ molecule in the first micro-solvation shell comprising a Kr₁₇ double icosahedron using numerical quantum-dynamic models as well as a linearized semiclassical IVR approach [X. Sun and W. H. Miller, *J. Chem. Phys.* **110**, 6635 (1999)]. We are trying to reproduce the experimental decoherence rates by making use of a reduced dimensionality model consisting of krypton ("bath") modes with different coupling to the I₂ vibrational ("system") mode.

This work was supported by the DFG through grant GR 1210/4-

2.

MO 6.6 Mon 17:45 V38.03

Weak field, multiple cycle carrier envelope phase effects in laser excitation — KLAUS RENZIEHAUSEN and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg

Whereas the absolute or carrier envelope phase (CEP) of a laser pulse is usually assumed to be effective for ultrashort and/or ultrastrong pulses only, we demonstrate that these limitations can be removed. For an initial population distribution between different states of a quantum system interacting with an external field, it is possible to influence the population transfer in changing the CEP. Analytical results for a two-level system are presented. In a numerical example, we treat molecular excitation, where vibrational manifolds in two electronic states of the sodium dimer are coupled by the laser field.

MO 6.7 Mon 18:00 V38.03

Carrier envelope phase controlled dynamics at conical intersections — ROBERT SIEMERING, PHILIPP VON DEN HOFF, and REGINA DE VIVIE-RIEDLE — Department Chemie Ludwig-Maximilians-Universität München, Butenandtstr. 11, Haus E, 81377 München, Germany

We investigate how ultrafast dynamics at conical intersection can be combined with laser control schemes. Therefore we study the effect of the non-adiabatic-coupling for wavepackets approaching the conical intersection from different directions and different momenta in model systems. These two dimensional model systems are set up in the g/h-plane (branching space) of the conical intersection between two potential energy surfaces. We analyse the relationship between transfer efficiency and the initial conditions of the wavepacket. Based on these results we develop a control scheme that relies on the carrier envelope phase of the control laser pulse. The control scheme includes the creation of an electronic superposition state before the wavepacket reaches the conical intersection. The control landscape is enhanced by applying optimal control strategies. To optimize carrier envelope phase control within optimal control theory we used its phase sensitive variant.

MO 6.8 Mon 18:15 V38.03

Efficient sub-cycle control of electron dynamics in molecules — HENDRIKE BRAUN¹, TIM BAYER¹, CRISTIAN SARPE¹, ROBERT SIEMERING², PHILIPP VON DEN HOFF², REGINA DE VIVIE-RIEDLE², MATTHIAS WOLLENHAUPT¹, and THOMAS BAUMERT¹ — ¹University of Kassel, Institute of Physics and CINSaT, D-34132 Kassel, Germany — ²Ludwig-Maximilians-Universität München, Department Chemie, D-81377 München, Germany

Shaped femtosecond laser pulses are a well established tool to control the dynamics of the nuclei within a molecule after electronic excitation. Here we demonstrate that the electron dynamics of a molecule can also be efficiently manipulated by controlling the temporal phase of a femtosecond laser pulse. Specifically, we show how temporal phase changes on the time scale of the electron motion, i.e. with sub-cycle precision, are used to manipulate the electron dynamics of molecules and eventually switch between different potential energy surfaces of the molecule. The underlying control mechanism is termed SPODS (Selective Population of Dressed States) and has already been demonstrated on atoms [1,2,3]. It relies on the resonant excitation of an *electronic* coherence and subcycle control of the phase relation of the corresponding electric dipole and the strong light field. Extension to molecular systems shows the prospect of various applications of SPODS in femtochemistry.

[1] M. Wollenhaupt *et al.*, *Phys. Rev. A* **68**, 0154011 (2003)

[2] M. Wollenhaupt *et al.*, *Phys. Rev. A* **73**, 063409-1 (2006)

[3] T. Bayer *et al.*, *Phys. Rev. Lett.* **102**, 023004 (2009)

[4] M. Wollenhaupt *et al.*, *JPPA* **180**, 248 (2006)

MO 6.9 Mon 18:30 V38.03

Selective population of dressed states: A robust pathway to populate selectively higher lying electronic states in molecules? — PHILIPP VON DEN HOFF¹, HENDRIKE BRAUN², TIM BAYER², MATTHIAS WOLLENHAUPT², THOMAS BAUMERT², and REGINA DE VIVIE-RIEDLE¹ — ¹Ludwig-Maximilians-Universität München, Department Chemie, Germany — ²University of Kassel, Institute of Physics and CINSaT, D-34132 Kassel, Germany

Selective population of dressed states (SPODS) has been proposed as an alternative control pathway in molecular reaction dynamics [1]. Re-

cently, this scenario was successfully implemented in experiments using the molecule K_2 . Based on these results, we investigate if and under which conditions this strong field scheme is included in the search space of optimal control theory (OCT). Thereby we classify SPODS within the global search space of OCT and discuss the question of robustness. Like in the experiments we use the example of the potassium dimer. Within the SPODS-mechanism different target states can be reached via dressed states by subcycle control of the phase relation of the corresponding electric dipole and the strong light field. Especially, we investigate whether the optimization algorithm is able to find the route involving the dressed states although the target state lies out of resonance in the bare state picture.

[1] M. Wollenhaupt *et al.*, Phys. Rev. A **68**, 0154011 (2003)

MO 6.10 Mon 18:45 V38.03

Attosecond dynamics of CO_2 and C_2H_4 — ●CHRISTIAN NEIDEL, JESSE KLEI, CHUNG-HSIN YANG, and MARC VRAKKING — Max-Born-Institut

We report the first attosecond time-resolved measurements for the molecules CO_2 and C_2H_4 . Angular resolved photoelectron and photoion yields were characterized with a velocity map imaging spectrometer (VMIS). Different fragments like O^+ and H^+ were produced by dissociative ionization. The signal yields show clear oscillations with respect to the time delay between an attosecond pulse train (APT) and a femtosecond IR pulse. The ionization process is modulated by coupling of molecular states by the IR field. The results demonstrate the feasibility of attosecond experiments for larger molecules.

MO 7: SYRA: Ultracold Rydberg Atoms and Molecules 1

Time: Tuesday 10:30–12:30

Location: V47.01

Invited Talk MO 7.1 Tue 10:30 V47.01
Quantum optics and quantum information with Rydberg excited atoms. — ●KLAUS MOLMER — Aarhus University, Aarhus, Denmark

The significant dipole-dipole interaction between Rydberg excited atoms provides an on/off controllable interaction with promising applications for entanglement operations and quantum computing with neutral atoms. The blockade interaction may be used to carry out quantum gate operations between individually addressed atomic qubits, and in small ensembles, the Rydberg blockade may simultaneously couple all atoms and thus enable quantum control of collective many-body state. On the one hand, this provides new efficient multi-bit schemes for quantum computing and, on the other hand, it gives access to non-classical states and interaction mechanisms in light-matter interfaces with applications in quantum optics and quantum communication.

Invited Talk MO 7.2 Tue 11:00 V47.01
Cooperative non-linear optics using Rydberg atoms — ●CHARLES ADAMS — Durham University, Durham, UK

The giant dipole associated with transitions between highly excited Rydberg states can be used to control the optical response of up to 1000 neighbouring atoms. This gives rise to a large cooperative optical non-linearity [1] that is effective at the single photon level providing the basis for fully deterministic all-optical quantum processing. In this talk we will discuss our recent progress in the area of Rydberg non-linear optics and present prospects for future developments.

[1] J. D. Pritchard *et al.* Phys. Rev. Lett. 105, 193603 (2010).

MO 7.3 Tue 11:30 V47.01
Rydberg electromagnetically induced transparency in dense ultracold gases — ●CHRISTOPH S. HOFMANN, GEORG GÜNTER, HANNA SCHEMP, HENNING LABUHN, MARTIN ROBERT-DE-SAINT-VINCENT, SHANNON WHITLOCK, and MATTHIAS WEIDEMÜLLER — Physikalisches Institut, Universität Heidelberg, Philosophenweg 12, 69120 Heidelberg

We report on our latest experimental results on Rydberg electromagnetically induced transparency performed in a regime which is governed by large Rydberg-induced nonlinearities. In these experiments the nonlinear optical response of a strongly interacting Rydberg gas is probed by means of a simple CCD camera. This work is a precursor experiment for realising direct optical images of Rydberg atoms [1]. The experiments are performed in our new apparatus which allows us to realise Bose-Einstein condensates (BECs) of ^{87}Rb for studies on Rydberg atoms excited from dense atomic gases. Starting with a high flux 2D-MOT, we efficiently load a MOT in order to pre-cool and efficiently transfer atoms into a crossed optical dipole trap. The latter acts as a reservoir that is superimposed with a dimple trap, in which we evaporatively cool the atoms to reach BEC. This simple and robust scheme allows us to perform experiments with short overall cycle times of only ~ 4.5 s.

[1] G. Günter *et al.*, arXiv:1106.5443v1 (2011) to be published in PRL

MO 7.4 Tue 11:45 V47.01
Electromagnetically Induced Transparency in Strongly Interacting Rydberg Gases — ●JOHANNES OTTERBACH¹, DAVID

PETROSYAN^{2,3}, ALEXEY V. GORSHKOV⁴, THOMAS POHL⁵, MIKHAIL D. LUKIN¹, and MICHAEL FLEISCHHAUER² — ¹Physics Department, Harvard University — ²Fachbereich Physik, TU Kaiserslautern — ³Institute of Electronic Structure and Laser, FORTH, Crete — ⁴Institute for Quantum Information, California Institute of Technology — ⁵Max Planck Institute for the Physics of Complex Systems, Dresden

The recent advance in coherently controlling and manipulating strong, long-range Rydberg interactions has triggered various studies of the Rydberg blockade effect for applications in quantum information processing and crystal formation. In this talk I show that Rydberg interactions can be used to alter the photon statistics of a weak probe field after propagating in a coherently prepared atomic Rydberg gas under conditions of Electromagnetically Induced Transparency (EIT). The Rydberg blockade mechanism leads to an effective two-level physics when two photons are separated less than the blockade radius resulting in a strong anti-correlation of two photons separated by an avoided volume. I argue that the formation of such hard-sphere photons is a key-ingredient in the explanation of the recent experiment of Pritchard *et al.* [Phys. Rev. Lett. 105, 193603 (2010)]. Finally the observation of such correlation in future experiments will be discussed.

MO 7.5 Tue 12:00 V47.01

Dipolar Bose-Einstein condensate of Dark-state Polaritons — ●GOR NIKOGHOSYAN¹, FRANK E. ZIMMER², and MARTIN B. PLENIO¹ — ¹Institut für Theoretische Physik, Albert-Einstein Allee 11, Universität Ulm, 89069 Ulm — ²Max Planck Institute for the Physics of Complex Systems, 01187 Dresden

We put forward and discuss in detail a scheme to achieve BEC of stationary-light dark-state polaritons with dipolar interaction. We extend the works on Bose-Einstein condensation of photons and polaritonic quasiparticles, to the regime of dipolar quantum gases. To this end we introduce a diamond-like coupling scheme in a vapor of Rydberg atoms under the frozen gas approximation. To determine the system's dynamics we employ normal modes and identify the dark-state polariton corresponding to one of the modes. We show that these polaritonic quasiparticles behave in adiabatic limit like Schrödinger particles with a purely dipolar inter-particle interaction. Moreover, we could show, by analyzing the Bogoliubov spectrum of a homogeneous dipolar BEC, that for a special choice of the dipolar interaction parameter the considered dipolar BEC is, in contrast to usual dipolar BEC, very stable.

MO 7.6 Tue 12:15 V47.01

Rydberg four wave mixing in a thermal gas of Rb — ●ANDREAS KÖLLE, GEORG EPPLE, THOMAS BALUKTSIAN, BERNHARD HUBER, HARALD KÜBLER, ROBERT LÖW, and TILMAN PFAU — 5. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart Germany

The Rydberg blockade effect is a promising candidate for use in quantum devices. In combination with a four wave mixing scheme a single photon source has been proposed. While ultracold gases seem to be the obvious choice, our vision is to use thermal atomic vapor in small glass cells which offers multiple advantages in terms of scalability and ease of use.

We present four wave mixing measurements including a Rydberg state in a thermal vapor cell and compare our results to a single atom

model. Furthermore we demonstrate the tunability of the four wave mixing scheme by means of an electric field via the Stark effect on the

Rydberg state.

MO 8: Photochemistry

Time: Tuesday 10:30–12:30

Location: V38.02

MO 8.1 Tue 10:30 V38.02

Single-molecule studies of photoswitchable organic triads — ●REGINA SCHMIDT¹, MARTTI PÄRS¹, CHRISTIANE HOFMANN¹, PETER BAUER², MUKUNDAN THELAKKAT², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — ²Applied Functional Polymers, University of Bayreuth, 95440 Bayreuth, Germany

We have investigated a triad, consisting of two perylenebisimide (PBI) fluorophores that are covalently linked to a photochromic dithienylcyclopentene (DCP) unit [1]. Converting the DCP between its two isomeric forms allows to modulate the PBI emission intensity of up to 80% of the signal level. Exploiting these features we have demonstrated on the ensemble level the potential of these triads to act as an optical transistor [2]. Here we will communicate our first steps to expand these experiments to the single-molecule level.

[1] M. Irie, *Chem. Rev.* 100, 1685-1716 (2000).

[2] M. Pärns, *Angew. Chem. Int. Ed.* 50, 11405-11408 (2011).

MO 8.2 Tue 10:45 V38.02

Control of photochromic molecules adsorbed to optical microfibres — ●ULRICH WIEDEMANN, WOLFGANG ALT, and DIETER MESCHÉDE — Institut für Angewandte Physik, Universität Bonn, Wegelerstraße 8, 53115 Bonn

The high light intensity on the surface of an optical microfibre can be used for strong light-matter interaction experiments with surface adsorbates. In previous experiments in our group ultra-sensitive absorption spectroscopy of surface-adsorbed organic dye molecules has been demonstrated [1]. After the passive observation of organic dyes, the next level of complexity is the optical manipulation of photochromic molecules. Switching between the molecular states is achieved by exposure to the evanescent field of a few nanowatts of UV or white light guided in the microfibre. The internal state of the molecules is detected via their state-dependent light absorption.

We present a quantitative analysis of the time-resolved photoswitching dynamics, which are measured and mathematically modelled with a rate equation model. By adjusting the microfibre evanescent field strength the dynamic equilibrium state of the molecules is controlled. Finally, we investigate how many times the photochromic system can be switched before undergoing significant photochemical degradation.

[1] F. Warken, E. Vetsch, D. Meschede, M. Sokolowski, and A. Rauschenbeutel, "Ultra-sensitive surface absorption spectroscopy using sub-wavelength diameter optical fibers," *Opt. Express* 15(19), 11952–11958 (2007).

MO 8.3 Tue 11:00 V38.02

Photochromic polypyridine ruthenium sulfoxide complexes on their way to condensed matters — ●KRISTIN SPRINGFELD, VOLKER DIECKMANN, SEBASTIAN EICKE, and MIRCO IMLAU — Department of Physics, University of Osnabrück, Germany

Creating new, more efficient data storage systems brings strong demand for materials that exhibit fast recording processes and long storage times. A promising approach are optical data storage devices that make use of photochromic molecules as storage materials, e.g., ruthenium polypyridine sulfoxides. They offer light-induced linkage isomerization at the SO-ligand accompanied with a pronounced UV/VIS photochromism, a tremendous photosensitivity and high thermal stability of the two metastable isomers. However, the field of applications is limited so far, because only molecular solutions are available. Here, we discuss the characteristic photochromic properties of the compounds in the frame of ligand substitution and replacement of the dielectric environment. The complex $[\text{Ru}(\text{bpy})_2(\text{ROSO})]\cdot\text{PF}_6$ [1] (with OSO: 2-methylsulfinylbenzoate) has been modified with several functional groups and was studied in different solvents as well as immobilized in an inorganic polymer. The analysis is performed by cw-pump-probe technique as a function of temperature and exposure. We discuss the impact of our findings in view of application in molecular photonic

devices.

Financial support by the DFG (INST 190/137-1) and the DAAD (50445542) is gratefully acknowledged.

[1] V. Dieckmann et al., *Opt. Express* 17, 15052 (2009)

MO 8.4 Tue 11:15 V38.02

Photoswitchable ruthenium sulfoxides and their adaptability for nonlinear molecular photonics — ●SEBASTIAN EICKE, SERGEJ BOCK, VOLKER DIECKMANN, KRISTIN SPRINGFELD, and MIRCO IMLAU — Department of Physics, University of Osnabrück, Germany

Ruthenium sulfoxides like $[\text{Ru}(\text{bpy})_2(\text{OSO})]^+$ (OSO: 2-methylsulfinylbenzoate) offer a light-induced linkage isomerization located at the SO-ligand resulting in pronounced changes of characteristic optical properties. These photoswitchable molecules are out-standing due to an ultrafast optical response in the ps range and a pronounced photochromism in the visible spectral range as well as long lifetimes in the metastable states. Furthermore, they can be simply tuned via ligand substitutions or different dielectric environments allowing for the adjustment of the spectral addressability, the magnitude of the absorption change and the generation/relaxation rates.

The talk gives a review on various molecule adaptabilities and presents a novel representative of the group of ruthenium sulfoxides whose optical properties have been successfully adjusted to the most common commercial laser sources. Thus the unique spectral addressability, the high efficient and the fast light-induced conversion of this new compound allow for applications in a multiplicity of devices. We particularly discuss their potential for ultrafast optical switches for controlling light by light and next-generation realtime holographic displays.

*Financial support by the DFG (INST 190/137-1) and DAAD (50445542) is gratefully acknowledged.

MO 8.5 Tue 11:30 V38.02

Ultrafast dynamics of photolyzed carbon monoxide in the primary docking site of hemoglobin, FixLH and R220H FixLH — ●PATRICK NUERNBERGER^{1,2}, KEVIN F. LEE¹, ADELINE BONVALET¹, LATIFA BOUZHIR-SIMA¹, JEAN-CHRISTOPHE LAMBRY¹, URSULA LIEBL¹, MANUEL JOFFRE¹, and MARTEN H. VOS¹ — ¹Laboratoire d'Optique et Biosciences, Ecole Polytechnique, CNRS, and INSERM U696, 91128 Palaiseau, France — ²Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

We report a mid-IR study of the ultrafast dynamics of CO in the docking site of the heme proteins hemoglobin, FixLH and the mutant R220H FixLH. We employ a recently developed chirped-pulse upconversion method that allows for simultaneous measurement of the absorption of both heme-bound and docked CO with high spectral resolution and sensitivity. The bacterial oxygen sensor FixLH displays marked differences in dynamic behavior upon ligand dissociation with respect to hemoglobin. We find that CO bound to the heme iron in FixL is tilted by $\approx 30^\circ$ with respect to the heme normal, which contrasts to the situation in globins and in present FixLH-CO X-ray crystal structure models. This implies protein environment-induced strain on the ligand, which is possibly at the origin of a very rapid docking site population in a single conformation. Our observations likely explain the unusually low affinity of FixL for CO that is at the origin of the weak ligand discrimination between CO and O₂.

MO 8.6 Tue 11:45 V38.02

Photosensitized generation of diphenylmethyl cations — ●SEBASTIAN THALMMAIR^{1,2}, CHRISTIAN F. SAILER¹, JOHANNES AMMER², EBERHARD RIEDLE¹, and REGINA DE VIVIE-RIEDLE² — ¹LS für BioMolekulare Optik, Ludwig-Maximilians-Universität München — ²Department Chemie, Ludwig-Maximilians-Universität München

Carbocations are omnipresent intermediates in organic chemistry as well as in biochemistry. Photoinduced bond cleavage of diphenylmethylphosphonium cations offers a convenient and very effective way to generate diphenylmethyl cations in both polar and moderately polar

solvents. An alternative route to the direct photoexcitation is to use a photosensitizer to induce the bond cleavage. We looked at anthracene as a possible candidate.

Its low energy absorption band ($\lambda \approx 360$ nm) is well separated energetically from the absorption bands of the precursor molecule ($\lambda \approx 280$ nm) and therefore gives the possibility to excite anthracene selectively in the presence of diphenylmethylphosphonium cations. Ultrafast broadband transient absorption measurements deliver insight into the evolution of the photoproducts from the femto- to the microsecond timescale. We can show that carbocations are generated from the S_1 state of anthracene. In contrast, the anthracene triplet seems to be unreactive.

Based on quantum chemical calculations performed for a phosphonium model system the mechanism of photosensitization will be discussed.

MO 8.7 Tue 12:00 V38.02

Towards ion molecule reactions in selected vibrational states — ●FABIAN HOCHHEIMER, MARTIN STEI, EDUARDO CARRASCOA, ADITYA KELKAR, THORSTEN BEST, and ROLAND WESTER — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck

The S_N2 mechanism is one of the fundamental chemical reaction mechanisms. Using cross beam velocity map imaging our group has verified the long proposed direct S_N2 mechanism in the reaction $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$ [1]. The text book picture involves an inversion of the CH_3 umbrella in the transition state [2]. As we could observe an efficient channeling of energy through the molecule, the question arises whether vibrational excitation of the umbrella mode acts as a spectator or influences the reaction. Using an IR-laser to prepare the molecular internal state prior to collision [3] may help to answer such questions. Here we report on our progress towards scattering of vibrationally excited CH_3I and Cl^- .

- [1] J. Mikosch, S. Trippel, C. Eichhorn, R. Otto, U. Lourderaj, J.X. Zhang, W.L. Hase, M. Weidemüller, R. Wester, *Science* 319, 183 (2008)
 [2] W. N. Olmstead, J. I. Brauman, *J. Am. Chem. Soc.*, 99 (1977)
 [3] W. Zhang, H. Kawamata, K. Liu, *Science* 325, 303 (2009)

MO 8.8 Tue 12:15 V38.02

Photodissoziation von fluorierten Acetonen nach Anregung in den S_1 -Zustand — ●THOMAS MICHALAK und FRIEDRICH TEMPS — Christian-Albrechts-Universität, Kiel

Die Photodissoziation von Aceton spielt für die Atmosphäre eine große Rolle, da die gebildeten Acetyl-Fragmente in einer Folgeraktion mit Luft OH-Radikale bilden. Während der wellenlängenabhängige Zerfall für Aceton weitestgehend untersucht ist, fehlen Untersuchungen zu fluorierten Derivaten. In dieser Arbeit wurde daher die Photodissoziation von Monofluoraceton (MFA), 1,1-Difluoroaceton (DFA) und 1,1,1-Trifluoroaceton (TFA) nach Anregung in den $S_1(n\pi^*)$ -Zustand im Wellenlängenbereich $\lambda = 333 - 240$ nm untersucht. Dazu wurde die Photofragment-Geschwindigkeitskartographie verwendet, die Aufschluss über die Energieverteilung der Fragmente und die Art und Anzahl der Dissoziationskanäle liefert. Detektiert wurde das CH_3 -Fragment. Die experimentellen Ergebnisse wurden durch quantenchemische Rechnungen unterstützt.

Der Dissoziationskanal zu $CH_3 + COCH_xF_y$ ist für $\lambda \leq 310$ nm (TFA), $\lambda \leq 300$ nm (DFA, MFA) offen. Analog zum Aceton erfolgt dieser Zerfall nach einem Intersystem Crossing und dem Überwinden einer Potentialbarriere im T_1 -Zustand. Sowohl die Barrierenhöhen als auch die Dissoziationsenergien der Kanäle konnten experimentell ermittelt werden. Wird die Wellenlänge noch weiter erniedrigt, wird ab $\lambda \leq 260$ nm (TFA), $\lambda \leq 275$ nm (DFA, MFA) auch CH_3 aus dem unimolekularen Zerfall des $COCH_3$ -Fragments detektiert, das aus dem primären Dissoziationskanal zu $CH_xF_y + COCH_3$ stammt.

MO 9: Femtosecond Spectroscopy II

Time: Tuesday 10:30–12:30

Location: V38.03

Invited Talk

MO 9.1 Tue 10:30 V38.03

The Interplay between Electron Transfer and Förster Resonant Energy Transfer — ●IGOR PUGLIESI¹, PATRICK KÖLLE², REGINA DE VIVIE RIEDLE², HEINZ LANGHALS², and EBERHARD RIEDLE¹ — ¹BioMolekulare Optik, LMU München — ²Dept. Chemie, LMU München

Energy and electron transfer are two fundamental processes on which the functioning of photoactive biological systems, solar cells and optoelectronic devices is based. The rates of these two processes can be described by Fermi's Golden Rule as they are both mediated by electronic coupling between donor and acceptor. This points to an intimate relation of energy and electron transfer on the electronic level. While energy transfer induced electron transfer has been observed in many artificial and biological systems, the inverse connection has not yet been investigated. Here we present an extended set of perylene diimide dyads with a donor-spacer-acceptor motif undergoing intramolecular FRET. Although the photoexcited donor is initially quenched by electron transfer from the spacer, after back transfer the energy of the donor is surprisingly transferred to the acceptor. Through broadband pump-probe measurements and high level ab-initio calculations we show that the donor-spacer electron transfer state itself is responsible for the energy transfer via multipole-multipole interactions with the locally excited state of the acceptor. The dyads presented here are a first example that shows how electron transfer can be connected to energy transfer for the use in novel photovoltaic and optoelectronic devices.

MO 9.2 Tue 11:00 V38.03

Time-resolved studies on the photoinduced electron transfer in mixed-valence donor-acceptor oligomers — ●FLORIAN KANAL¹, STEFAN RUTZEL¹, HAN LU², CHRISTOPH LAMBERT², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Mixed-valence triarylamine-donor-triarylmethyl-acceptor compounds are interesting model systems for investigating photoinduced electron

transfers. These compounds possess a broad absorption band in the near infrared spectral region originating from an intervalence charge transfer (IVCT).

Here, we present femtosecond transient absorption experiments on two different alternating donor-acceptor triads consisting of a donor-acceptor-donor and an acceptor-donor-acceptor pattern. For comparison the respective donor-acceptor subunit as well as the subunit dimer were also investigated. By using the output of an amplified Ti:Sapphire femtosecond laser one can pump the systems directly into the IVCT state. The reduced acceptor as well as the oxidized donor show typical transient absorption bands, which are probed with a whitelight supercontinuum. The molecular dynamics are unraveled by a global data fitting procedure. Environment-dependent contributions of the dynamics are identified by performing the experiments in solvents of different polarity.

MO 9.3 Tue 11:15 V38.03

Impact of High Excitation Densities upon Excitons in Perylene Bisimide Aggregates — ●MARCUS SEIDEL, STEFFEN WOLTER, and STEFAN LOCHBRUNNER — Universität Rostock, Institut für Physik, Universitätsplatz 3, 18055 Rostock

Transient absorption measurements are performed on substituted Perylene Bisimide Aggregates with intense pump pulses that clearly saturate the ground state absorption of the molecules. The investigated Perylene Bisimides form J-aggregates at room temperature if solved in a nonpolar solvent with sufficiently high concentration [1]. Since the fluorescence quantum yield and the exciton diffusion length of these aggregates are high [1,2], they might be very suitable components for optoelectronic devices such as organic solar cells. Exciton-Exciton-Annihilation has been observed as the dominating interaction at moderately high excitation densities [2]. Although the interaction itself is not known in detail, it is assumed that two- and multi-excitonic states, resp. play an important role in the light induced dynamics of the quasi-particles. In a first approach to detect these multi-excitonic states in fs-pump-probe measurements, intense laser pulses are utilized to generate high excitation densities. The corresponding transient absorption spectra reveal a fast decaying component, which is considered as a multi-excitonic state signature.

[1] Li X.-Q., Zhang X., Ghosh S., Würthner F., Chem. Eur. J. 14, p.8074 - p.8078 (2008)

[2] Marciniak H., Li X.-Q., Würthner F., Lochbrunner S., J. Phys. Chem. 115, p.648 - p.654 (2011)

MO 9.4 Tue 11:30 V38.03

Ultrafast emission quenching in a perylene diimide by structure rearrangement induced electron transfer from its substituent — ●PATRICK KÖLLE¹, ARTUR NENOV¹, UWE MEGERLE², PATRIZIA KROK², HEINZ LANGHALS¹, REGINA DE VIVIE-RIEDLE¹, and EBERHARD RIEDLE² — ¹Ludwig-Maximilians-Universität München, Department Chemie, Germany — ²Ludwig-Maximilians-Universität München, Lehrstuhl für BioMolekulare Optik, Germany

The ultrafast excited-state dynamics of the fluorescent perylene diimide chromophore and its non-fluorescent amino-functionalized derivative are investigated by transient spectroscopy and quantum chemical calculations. The fluorescent system shows no dynamics in the sub-nanosecond time region. For the functionalized molecule the stimulated emission signal decays rapidly on a sub-picosecond timescale, while the excited state absorption decreases with a time constant of several picoseconds. The theoretical analysis assigns the fast decay to a charge transfer from the amino substituent to the perylene diimide chromophore. The transfer is made possible by a decrease of the N-N distance and a planarization of the substituent as the system moves away from the Franck-Condon point. Experiments in different solvents demonstrate that the dynamics of this fluorescence quenching correlate with the solvation time. The rapid relaxation from the charge transfer state into the ground state is observed on a picosecond timescale and is attributed to a passage through a conical intersection.

MO 9.5 Tue 11:45 V38.03

Introducing a new concept to understand excited state dynamics in polyenes: The dynamophore — ●OLIVER SCHALK^{1,2}, ANDREY E. BOGUSLAVSKIY¹, MICHAEL S. SCHURMAN¹, EBERHARD RIEDLE², and ALBERT STOLOW¹ — ¹SIMS, Ottawa, Canada — ²BioMolekulare Optik, LMU, München

In organic molecules, UV- and vis-photons are absorbed by a chromophore, which constitutes the part of a molecule where the electronic transition for a given spectral band is localized. However, the dynamics induced by these photons may take place in a distinct region of the molecular framework. We define this region as dynamophore, i.e. the entity where the nuclear dynamics upon light absorption are mainly localized. This concept allows for systematizing recurring patterns in the relaxation pathway of different molecules and provides the possibility to develop a simplified model for the photodynamics. In this presentation, we elaborate on this new concept and show first examples from our time resolved photoelectron studies and *ab initio* calculations on small polyenes such as butadiene, cyclopentadiene [1], and cyclohexa-1,4-diene [2]. These examples emphasize a trend toward the localization of excited state dynamics, and illustrate the importance of Franck-Condon active modes in the selection of a specific

dynamophore.

[1] O. Schalk *et al.* J. Phys. Chem. A **114**, 4508 (2010).

[2] O. Schalk *et al.* J. Am. Chem. Soc. **131**, 16451 (2011).

MO 9.6 Tue 12:00 V38.03

Reaction Dynamics of a Molecular Switch Unveiled by Coherent Two-Dimensional Electronic Spectroscopy — ●MARTIN KULLMANN, STEFAN RUETZEL, JOHANNES BUBACK, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Coherent two-dimensional electronic spectroscopy is usually employed on molecular species with fixed geometric configuration. Here we present two-dimensional Fourier-transform electronic spectra of dissolved 6,8-dinitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline], a photochromic system present in two ring-open forms which differ by a cis/trans configuration of a double bond. Both isomers undergo a photo-induced ring closure.

The two-dimensional spectra, recorded with 20 fs pump pulses centered at 605 nm and a supercontinuum probe covering the complete visible spectral range, allow for a detailed analysis of the photophysics and photochemistry of the two isomers, and directly reveal that cis/trans isomerization among them does not play a major role [1]. This experiment demonstrates the potential of two-dimensional electronic spectroscopy for reactive processes.

[1] M. Kullmann, S. Ruetzel, J. Buback, P. Nuernberger, and T. Brixner, J. Am. Chem. Soc. **133**, 13074, (2011).

MO 9.7 Tue 12:15 V38.03

Femtosecond Pump-Probe Scanning Near-Field Optical Microscopy (PP-SNOM): Sub-Wavelength Resolution Chemical Imaging and Local Dynamics — ●TAHIR ZEB KHAN, KHADGA J. KARKI, MAHESH NAMBOODIRI, and ARNULF MATERNY — Research Center for Functional Materials and Nanomolecular Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany

Femtosecond time-resolved pump-probe (PP) spectroscopy techniques allow for the investigation of ultrafast dynamics of molecules. Scanning near-field optical microscopy (SNOM) is capable of generating images with spatial resolution below diffraction limit. In our work, we have combined these two techniques enabling us to record nanoscale images non-invasively along with chemical specificity and local probing of the molecular dynamics. We present results of PP-SNOM investigations of thin films of the organic semiconductor 3,4,9,10 perylene tetra carboxylic dianhydride (PTCDA). The exciton dynamics of a 160 nm thick PTCDA layer composed of nano-crystals on glass was locally probed with a SNOM tip allowing for 100 nm spatial resolution. Intensity-dependent exciton dynamics observed at exciton densities higher than 10^{19} cm^{-3} is attributed to exciton-exciton annihilation. Differences found for the annihilation constant found in far and near-field investigations are discussed.

MO 10: SYRA: Ultracold Rydberg Atoms and Molecules 2

Time: Tuesday 14:00–16:00

Location: V47.01

Invited Talk

MO 10.1 Tue 14:00 V47.01

Ultralong-range Rydberg molecules — ●THOMAS POHL — MPI for the Physics of Complex Systems, Dresden, Germany

Ultralong-range Rydberg molecules represent an extreme and peculiar example of chemical binding, where a ground state atom is bound inside the electronic wave function of a highly excited Rydberg atom. Owing to their large bond length of several thousand Bohr radii, these molecules - first produced in 2009 [1] - exhibit several unusual properties, some of which will be discussed in this talk.

Following a simplified discussion of the basic interaction mechanisms, I will describe more sophisticated calculations, which reveal, yet, another new binding mechanism based on internal quantum reflection [2]. Good agreement with experiments on ultracold Rubidium molecules, gives strong indication that the predicted molecular states indeed provide a manifestation of such elementary quantum phenomena. A close look at small-electric field effects uncovers the existence of a sizable molecular electric dipole moment [3], which comes as a surprise for homo-nuclear molecules.

Besides being of fundamental interest, such exotic molecules turn out to be also of relevance to other Rydberg-atom settings. In order to illustrate this point, I will consider their collective excitation dynamics in mesoscopic ultracold gases and discuss possible implications for ensemble-based quantum information/optics applications.

[1] V. Bendkowsky *et al.*, Nature (London) **458**, 1005 (2009)

[2] V. Bendkowsky *et al.*, Phys. Rev. Lett. **105**, 163201 (2010)

[3] W. Li *et al.*, Science **334**, 1110 (2011)

Invited Talk

MO 10.2 Tue 14:30 V47.01

Quantum Information Processing with Rydberg Atoms — ●PHILIPPE GRANGIER — Institut d'Optique, RD128, 91127 Palaiseau, France

We will present an overview of the use of direct interactions between trapped cold Rydberg states for quantum information processing.

A first approach is to use dipole blockade between individually trapped atoms, used as quantum bits. This allows one to generate entangled pairs of atomic qubits, and to perform quantum gates, as it has been demonstrated by several recent experiments that will be

presented.

A second approach is to use atomic ensembles, and to excite Rydberg polaritons in order to generate "giant" optical non-linear effects, that may lead to quantum gates for photonic qubits. Perspectives in that direction will be also discussed.

MO 10.3 Tue 15:00 V47.01

Electric field impact on ultra-long-range triatomic polar Rydberg molecules — ●MICHAEL MAYLE¹, SETH T. RITTENHOUSE², PETER SCHMELCHER³, and HOSSEIN R. SADEGHPOUR² — ¹JILA, University of Colorado Boulder and NIST, USA — ²ITAMP, Harvard-Smithsonian Center for Astrophysics, USA — ³Zentrum für Optische Quantentechnologien, Universität Hamburg

We explore the impact of external electric fields on a recently predicted species of ultra-long-range molecules that emerge due to the interaction of a ground state polar molecule with a Rydberg atom. The external field mixes the Rydberg electronic states and therefore strongly alters the electric field seen by the polar diatomic molecule due to the Rydberg electron. As a consequence the adiabatic potential energy curves responsible for the binding can be tuned in such a way that an intersection with neighboring curves occurs. The latter leads to an admixture of *s*-wave character to the Rydberg wave function and should significantly facilitate the experimental preparation of this novel species.

MO 10.4 Tue 15:15 V47.01

Supersymmetry in Rydberg-dressed lattice fermions — ●HENDRIK WEIMER¹, LIZA HUIJSE¹, ALEXEY GORSHKOV², GUIDO PUPILLO³, PETER ZOLLER⁴, MIKHAIL LUKIN¹, and EUGENE DEMLER¹ — ¹Physics Department, Harvard University, Cambridge, MA, USA — ²IQI, Caltech, Pasadena, CA, USA — ³University of Strasbourg, Strasbourg, France — ⁴University of Innsbruck and IQOQI, Innsbruck, Austria

Supersymmetry is a powerful tool that allows the characterization of strongly correlated many-body systems, in particular in the case of supersymmetric extensions of the fermionic Hubbard model [1]. At the same time, these models can exhibit rich and exotic physics on their own, such as flat bands with a vanishing dispersion relation. We show that such lattice models can be realized with Rydberg-dressed fermions in optical lattices. Strong interactions within the ground state manifold of the atoms can be realized by admixing a weak contribution of a highly excited Rydberg state [2]. We discuss the unique possibilities of ultracold atoms for the detection of supersymmetry and the effects of tuning the system away from the supersymmetric point.

- [1] P. Fendley, K. Schoutens, J. de Boer, PRL **90**, 120402 (2003).
[2] J. Honer, H. Weimer, T. Pfau, H. P. Büchler, PRL **105**, 160404 (2010).

MO 10.5 Tue 15:30 V47.01

Aufbau eines Experiments zur Rydberganregung von ⁴⁰Ca⁺ Ionen — ●THOMAS FELDKER, JULIAN NABER, FERDINAND SCHMIDT-KALER, DANIEL KOLBE, MATTHIAS STAPPEL und JOCHEN WALZ — Quantum, Institut für Physik, Johannes Gutenberg Universität, Mainz

In Paulfallen gefange, lasergekühlte Ionen gehören zu den vielversprechendsten Kandidaten für die Quanteninformationsverarbeitung, während hoch angeregte Rydbergzustände und die damit verbundene Dipol-Blockade zu den interessantesten Entwicklungen der letzten Jahre in der Atomphysik gehören. Wir vereinen diese Ansätze, indem wir ⁴⁰Ca⁺ Ionen in einer Paulfalle in Rydbergzustände anregen [1,2]. Ziel ist die Spektroskopie von Rydbergzuständen einzelner Ionen im dynamischen Potential der Paulfalle und die Erzeugung von Vielteilchen-Verschränkung in Ionenkristallen.

Wir fangen und kühlen ⁴⁰Ca⁺ in einer linearen Paulfalle. Die kalten Ionen sollen in den metastabilen ³D_{5/2} Zustand angeregt werden, aus dem sie mit Laser-Licht bei 123 nm in einen Rydbergzustand angeregt werden können.

- [1] F. Schmidt-Kaler, T. Feldker, D. Kolbe, J. Walz, M. Müller, P. Zoller, W. Li and I. Lesanovsky, New J. Phys., 2011 [2] M. Müller, Linmei Liang, Igor Lesanovsky and Peter Zoller, New J. Phys., 2008

MO 10.6 Tue 15:45 V47.01

Strongly interacting single photons in an ultra-cold Rydberg gas — STEPHAN JENNEWEIN, HUAN NGUYEN, MICHAEL SCHLAGMÜLLER, CHRISTOPH TRESP, and ●SEBASTIAN HOFFERBERTH — 5. Phys. Institut, Universität Stuttgart

Strong photon-photon coupling can in principle be achieved inside extremely nonlinear media. The search for few-photon nonlinearities is a highly active field, including such diverse systems as quantum dots, NV centers in diamond, atomic ensembles, and single atoms in optical resonators. However, no robust and scalable realization of, for example, a single-photon switch has been achieved so far. Here, we present a new approach that aims to realize dramatically enhanced photon-photon interactions by mapping quantum correlations between strongly interacting atoms inside an ultra-cold gas onto single photons. We show that this technique can be used to implement building blocks for photonic quantum information processing, such as a deterministic single-photon source and a quantum phase gate.

MO 11: Biomolecules

Time: Tuesday 14:00–16:00

Location: V38.02

MO 11.1 Tue 14:00 V38.02

The Sugar Ribose - Structural Complexity in the Gas Phase — E. J. COCINERO¹, P. ÉCIJA¹, F. BASTERRETXEA¹, J. A. FERNÁNDEZ¹, F. CASTAÑO¹, A. LESARRI², and ●J.-U. GRABOW³ — ¹Universidad del País Vasco, Bilbao, Spain — ²Universidad de Valladolid, Valladolid, Spain — ³Gottfried-Wilhelm-Leibniz-Universität, Hannover, Germany

Sugars are cellular energy fuels, metabolic intermediates, mediators of cellular interactions and structural building blocks. Recently sugars moved into the focus of the quest for prebiotic building blocks in the interstellar medium as tracer for the construction of molecular complexity. However, sugars are structurally complex and elusive to experimental methods: the C5 D-aldose sugar, ribose, was only elucidated by X-ray crystal diffraction in 2010, but the structural information is biased by crystal packing forces. NMR methods conducted in condensed phases yield only solvent-averaged indirect structures.

In textbooks ribose is usually depicted as a β -furanose, predominant in ribonucleosides, ARN, ATP and other biochemically relevant derivatives. But is β -furanose the native form of free ribose? In order to solve these questions we conducted a rotational study of ribose combining FTMW spectroscopy in supersonic jets with ultrafast UV laser vaporization. We could detect six low-energy conformers, all belonging to the pyranose motif; in energetic order: *cc*- β -pyr ¹C₄, *cc*- β -pyr ⁴C₁, *c*- β -pyr ¹C₄, *c*- α -pyr ¹C₄, *cc*- α -pyr ¹C₄, *c*- α -pyr ⁴C₄. As given, the method also allows for unambiguous distinction between different

orientations - clockwise/counterclockwise - of the hydroxyl groups.

MO 11.2 Tue 14:15 V38.02

Monitoring Potential Molecular Interaction Pathways between Adenine and Amino Acids (Gly, Lys, Arg) Using Raman Spectroscopy and DFT Modeling — ●PATRICE DONFACK¹, SHWETA SINGH^{1,2,4}, SUNIL K. SRIVASTAVA^{1,3,4}, SEBASTIAN SCHLÜCKER⁴, PHOOL C. MISHRA², BIRENDRA P. ASTHANA², and ARNULF MATERNY¹ — ¹Research Center for Functional Materials and Nanomolecular Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany — ²Department of Physics, Banaras Hindu University, Varanasi 221005, India — ³Department of Pure and Applied Physics, Guru Ghasidas Vishwavidyalaya, Main Campus, Koni, Bilaspur-495009, India — ⁴Fachbereich Physik, Universität Osnabrück, BarbarasträÙe 7, D-49076 Osnabrück, Germany

In this contribution, we report on Raman spectroscopy and DFT calculations on binary mixtures of adenine with the amino acids Gly, Lys, and Arg at varying molar ratios. We have observed specific changes in the Raman bands of adenine due to the presence of the amino acids. While this is less apparent in the adenine/Gly system, in for Lys or Arg consistent changes are observed in the adenine bands that involve the amino (-NH₂) moiety and the ring N-7 and N-9. Conclusions can be drawn on the interactions between adenine and Lys or Arg proving to be sensitive to both protonation and hydrogen bonding properties. A clear indication is provided that whether the adenine interacts with an amino acid strongly depends on the chemical structure of the latter.

DFT calculations have been carried out to further elucidate realistic interaction schemes of adenine with the amino acids.

MO 11.3 Tue 14:30 V38.02

Excited states lifetimes of riboflavin derivatives in solution — ●YVONNE SCHMITT¹, MADINA MANSUROVA², WOLFGANG GÄRTNER², and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, Physikal. & Theoret. Chemie, 67663 Kaiserslautern — ²MPI für Bioanorganische Chemie, 45470 Mülheim a. d. Ruhr

Riboflavin has a wide spread field of applications in biology. It reaches from human beings where it is a part of the FAD and FMN, to animals where it is part of the so called cryptochromes and plants in which it supports the execution of photosynthesis. From the spectroscopic point of view riboflavin has interesting features because it can exist in three redox states and different electronic states with different structures. The free rotating ribityl chain can lead to different isomers and it is in discussion if these different build ups of riboflavin are important for its functionality. To characterize different electronic states and structures of the molecule infrared, absorption, fluorescence and fluorescence lifetime measurements are applied in addition to quantum mechanical calculations. In this contribution the attention is turned to derivatives of riboflavin since riboflavin exists in nature mostly in a modified form. The electronically excited states and their lifetimes are characterized in different solvents and compared to the spectroscopic features of pure riboflavin.

MO 11.4 Tue 14:45 V38.02

IR-MPD and H-/D-exchange studies on aspartame (Asp-Phe-OMe) and Asp-Phe — ●LARS BARZEN¹, CHRISTINE MERKERT¹, FABIAN MENGES¹, YEVGENIY NOSENKO¹, GEREON NIEDNER-SCHATTEBURG¹, PHILIPPE MAITRE², and JEAN-MICHEL ORTEGA² — ¹TU Kaiserslautern, Fachbereich Chemie, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern, Germany — ²CLIO/LCP, Université Paris-Sud 11, 91405 Orsay Cedex, France

Aspartame (Asp-Phe-OMe), which is a well known sweetener, and its unprotected analog Asp-Phe have been investigated in the gas phase in the form of protonated cations, of deprotonated anions and of alkali metal cation adducts. We recorded infrared multiphoton dissociation (IR-MPD) spectra of protonated and deprotonated aspartame and Asp-Phe in the range of 2200 - 3900 cm⁻¹ by a Laservision IR-OPO system and of protonated and deprotonated aspartame in the range of 600 - 1800 cm⁻¹ through application of the Free Electron Laser (FEL) CLIO in Orsay, Paris. For the protonated and deprotonated species and for the alkali metal ion adducts (Li-Cs) of both peptides the most stable structures and IR-spectra have been calculated at DFT level (B3LYP//cc-pVDZ/Stuttgart RSC 1997) and have been compared with respect to their alkali binding sites. H-/D-exchange studies of the protonated and of the alkali metal attached species (Li-K) with ND₃ in our 7-T-Bruker-FT-ICR mass spectrometer give information on the number of easily accessible / available acidic protons and therefore help to elucidate the structure of these molecules. These results are compared to the calculated minimum structures.

MO 11.5 Tue 15:00 V38.02

IR/UV investigations of isolated β -turn and β -sheet peptides — ●KIRSTEN SCHWING¹, THOMAS SCHRADER², and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, Physikal. und Theoret. Chemie, 67663 Kaiserslautern — ²Universität Duisburg-Essen, Organische Chemie, 45117 Essen

Due to the direct correlation between structure and functionality of biomolecules the structural investigation of peptides is of great scientific interest. Beyond the influence from the peptide environment intrinsic properties as amino acid sequence and secondary structure are of high importance for conformational preferences. The latter can be studied in molecular beam experiments with combined IR/UV spectroscopy as well as DFT calculations. This strategy is applied to two tripeptide models containing the aromatic amino acids phenylalanine and tyrosine (Ac-Phe-Tyr(Me)-NHMe and Boc-Phe-Tyr(Me)-NHMe). Both species prefer β -turn-structures energetically favoured by aromatic π ... π interactions, whose impact on the stability of secondary structures has been revealed for biological systems. Further important secondary structure motifs are β -sheets, whose formation in the brain tissue is involved in the pathogenesis of different neurodegenerative diseases. Here we describe the first IR/UV analysis of an isolated hetero dimer in a molecular beam. The chosen systems Ac-Val-Tyr-

NHMe and Ac-Ala-Ala-Ala-OMe can form different binding motifs as isolated monomer species but the hetero dimer gives a clear evidence of a β -sheet arrangement indicating driving forces for specific structural preferences in isolated peptides.

MO 11.6 Tue 15:15 V38.02

Light triggered peptide folding: Beta-hairpin formation on the nano to microsecond timescale. — ●ANDREAS DEEG¹, MICHAEL RAMPP¹, TOBIAS E. SCHRADER¹, JOSE PFIZER², LUIS MORODER², and WOLFGANG ZINTH¹ — ¹BioMolecular Optics, University of Munich, Germany — ²Max-Planck-Institut für Biochemie, Martinsried, Germany

The formation of secondary structure elements like alpha-helices or beta-hairpins are still a matter of intense scientific interest. We have investigated the folding mechanism of a beta-hairpin structure with a model peptide containing two amino acid strands connected by an azobenzene switch in the centre. The peptide forms a beta-hairpin when the azobenzene is in the cis conformation and a random structure for azobenzene in trans [1]. Recently the light triggered unfolding of the beta-hairpin has been investigated and the unfolding was observed within 3ns [2]. In this contribution the folding of the peptide was studied by time resolved vibrational spectroscopy on the nano to microsecond timescale for different temperatures. We observed strongly temperature dependent single exponential folding dynamics on the 10-100 microsecond timescale. A folding mechanism and an energy landscape, consistent with our data are discussed.

[1] S.-L Dong, Chem.Eur.J. 12, 1114-1120 (2006)

[2] T.E. Schrader, PNAS 104, 15729-15734 (2007)

MO 11.7 Tue 15:30 V38.02

Rotationally resolved electronic spectroscopy of a flexible biomolecule: melatonin — ●MICHAEL SCHMITT¹, CHRISTIAN BRAND¹, W. LEO MEERTS², and DAVID W. PRATT³ — ¹Heinrich-Heine-Universität Düsseldorf — ²Radboud University Nijmegen — ³University of Pittsburgh

Rotationally resolved electronic spectra of two origin bands of melatonin have been analyzed using an evolutionary strategy approach. From a comparison of the *ab initio* calculated structures of energy selected conformers to the experimental rotational constants, one band could be shown to be due to a gauche structure of the side chain, while the other band is due to an anti structure. Both bands show a splitting from the three-fold internal rotation of the methyl rotor in the N-acetyl group of the molecules. From a torsional analysis we additionally were able to determine the barriers of the methyl torsion in both electronic states. The electronic nature of the lowest excited singlet state could be determined to be L_b (as in the chromophore indole) from comparison to the results of *ab initio* calculations.

MO 11.8 Tue 15:45 V38.02

Multiplex-CARS microspectroscopy as a tool for fast characterisation of ligno-cellulosic biomass — ●CHRISTOPH POHLING¹, CHRISTIAN BRACKMANN², TIAGO BUCKUP¹, ANNIKA ENEJDER², and MARCUS MOTZKUS¹ — ¹PCI, Uni Heidelberg, Germany — ²Dep. of Chemical and Biological Engineering, Chalmers University, Göteborg, Sweden

Wood biopolymers such as cellulose and lignin have strong potential to replace petroleum-based sources for synthesis of chemicals and materials. This development requires efficient characterization of these renewable raw products, especially in industrial processing where measurement speed is an important factor. Raman microspectroscopy detects sample components probing molecular vibrations. However, the method is time consuming and a pixel dwell time of 500 ms is often necessary in case of biological samples. In this work acquisition time has been reduced using the non-linear Raman-based technique multiplex coherent anti-Stokes Raman scattering (MCARS) microscopy. Wood samples have been investigated using a data acquisition time of 60 ms per pixel and MCARS provided excellent image contrast, background-free chemical imaging and quantitative results. Data analysis using the maximum entropy method (MEM) gave Raman-equivalent data on sample composition and polarization control of the excitation beams provided additional information on the molecular orientation of the wood fibers. In total, MCARS turned out to be a very suitable tool for material characterization, providing rapid imaging with quantitative measures of sample composition and structural information.

MO 12: Femtosecond Spectroscopy III

Time: Tuesday 14:00–16:00

Location: V38.03

Invited Talk

MO 12.1 Tue 14:00 V38.03

New insights into solution-phase chemistry under ambient conditions via ultrafast X-ray spectroscopy — ●NILS HUSE — Ultrafast Molecular Dynamics Group, Max Planck Research Department for Structural Dynamics at the University of Hamburg & Center For Free Electron Laser Science, Hamburg, Germany

The high chemical specificity and localized nature of core-level transitions combined with their sensitivity to valence charge distribution, spin-state, and nuclear motion make transient X-ray spectroscopy a powerful method to study chemical reactions. In particular, solution-phase chemistry has been investigated with time-resolved hard X-ray techniques for the past decade [1-3]; its younger soft X-ray analogue has delivered first results more recently [4-7]. Moreover, the first transient spectroscopy of aqueous solution in the X-ray water window demonstrates the feasibility of studying ultrafast processes via the Nitrogen K-edge. With attosecond sources approaching the necessary photon energies, this type of spectroscopy will allow to follow charge migration and successive chemical reactions in water with the chemical specificity and atomic resolution intrinsic to core-level transitions.

1. Chen et al., *Science* 292, 262 (2001); 2 Bressler et al., *PRL* 90, 047403 (2003); 3. Khalil et al., *JPCA* 110, 38 (2006); 4. Wernet et al., *APA* 92, 511 (2008), Huse et al., *PCCP* 11, 3789 (2009); 5. Wen et al., *JCP* 131, 234505 (2009); 6. Huse et al. *JACS* 132, 6809 (2010); 7. Huse et al. *JPCL* 2, 880 (2011).

MO 12.2 Tue 14:30 V38.03

Dynamics and structure in hydrogen bonded systems probed with resonant inelastic soft x-ray scattering — ●SIMON SCHRECK¹, KRISTJAN KUNNUS¹, WILSON QUEVEDO¹, FRANZ HENNIES², BRIAN KENNEDY², SIMONE TECHERT³, PHILIPPE WERNET¹, and ALEXANDER FÖHLISCH¹ — ¹Helmholtz-Zentrum Berlin — ²MAX-lab — ³Max-Planck-Institut BPC, Göttingen

Hydrogen bonded systems are ubiquitous in nature ranging from bonding in DNA to liquid water as a solvent and the natural medium for many chemical reactions and proteins. Often the structure and function of molecules and proteins is determined by the bonding properties in these systems. On the other hand the structure and the dynamics even of the simplest hydrogen bonded systems such as water and methanol are still the subject of controversial discussions.

We used resonant inelastic soft x-ray scattering (RIXS) at the O K-edge to study the dynamics and structure of liquid water and methanol. RIXS is an element specific and local probe of the valence electronic structure and hence very sensitive to the local geometric structure. Since the scattering process takes place in only a few femtoseconds (fs), RIXS is sensitive to dynamics on the fs-timescale. By detuning below the absorption resonance, the scattering-duration time can be reduced significantly and even shorter timescales can be investigated. Studying the angular anisotropy of the scattered photons gives information about the symmetry of the involved states.

The measurements were performed at the synchrotron radiation source BESSYII at the Helmholtz-Zentrum Berlin.

MO 12.3 Tue 14:45 V38.03

ESIPT in 3-Hydroxyflavone and 3-Hydroxychromone: A Femtosecond Transient Absorption Study — ●KATHARINA CHEVALIER¹, MATTHIAS M.N. WOLF¹, ANDREAS FUNK³, MARKUS GERHARDS² und ROLF DILLER¹ — ¹Dept. of Physics, Univ. Kaiserslautern — ²Dept. of Chemistry, Univ. Kaiserslautern, 67663 Kaiserslautern, Germany — ³Institute for Buildings and Materials Chemistry, Univ. Siegen, 57076 Siegen, Germany

3-Hydroxyflavone (3HF) and its derivatives have recently gained interest as fluorescent probes in micelles, liposomes and membranes. Since the respective time constant of proton transfer after electronic excitation (ESIPT) with UV light as well as the characteristics of the fluorescence and transient absorption depend strongly on the polarity and hydrogen bonding ability of the surrounding medium it is important to understand the mechanism of energy deactivation. 3-hydroxychromone (3HC) is one of the basic chromophoric units of naturally occurring flavonoids which can form an intramolecular hydrogen bond. Studies in gas phase and in hydrocarbon solution have revealed a proton transfer in the excited state similar to 3HF but with significant differences in the emission properties. Results from condensed phase sub-picosecond

time resolved absorption spectroscopy are presented and compared to quantum chemical calculations allowing for the identification and characterization of photoinduced processes and intermediate states.

MO 12.4 Tue 15:00 V38.03

Ultrafast solvation dynamics of ferulic acid at a micellar surface — ●MAYRA STUHLREIER¹, MICHAL MALICKI¹, HENDRIK BÖHNKE¹, KATHLEEN OEHLKE², KARIN SCHWARZ², and FRIEDRICH TEMPS¹ — ¹Institute of Physical Chemistry, Christian-Albrechts-University Kiel, D-24118 Kiel — ²Department of Food Technology, Christian-Albrechts-University Kiel, D-24118 Kiel

The solvation dynamics of the anti-oxidant ferulic acid (FA) in buffered aqueous solution and in the palisade layer of CTAB micelles have been investigated by means of femtosecond time-resolved broadband fluorescence spectroscopy. Since the dipole moment of the molecules increases significantly upon electronic excitation, the solvent shell around the excited molecule in solution will rearrange to reach the energetically most favourable position according to the new dipole moment. This reorganization can be monitored by recording the emission spectra shortly after excitation, as they show a time-dependent red-shift corresponding to the stabilization of the solvated excited molecule. The time that is needed to reach the equilibrium structure of the solvated excited molecule and hence to complete the fluorescence shift is directly related to the mobility of the solvent molecules and therefore to the structure of the microenvironment of the solvated molecule. Compared with the dynamic red-shift of the emitted fluorescence in bulk water, a deceleration of the solvation dynamics of FA in micellar environment is clearly observable. This difference is attributed to the fast reorientation of the water molecules around the excited solutes, which is sterically hindered at the micellar surface.

MO 12.5 Tue 15:15 V38.03

Femtosecond mid-infrared study on the photochemistry of a CO-releasing compound in water — ●PHILIPP RUDOLF¹, FLORIAN KANAL¹, DOMINIK GEHRIG¹, JOHANNA NIESEL², TOBIAS BRIXNER¹, ULRICH SCHATZSCHNEIDER², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

In recent years, biological applications of CO-releasing molecules (CORMs), which may be utilized as an in-situ source for carbon monoxide, an endogenous gasotransmitter in the human body, have been demonstrated. Especially promising are water-soluble metal carbonyl complexes which can act as dark-stable prodrugs under physiological conditions. One of these compounds is the [Mn(CO)₃(tpm)]Cl (tris(pyrazolyl)methane (tpm) manganese tricarbonyl) complex which undergoes photoinduced CO release upon UV irradiation.

So far, the carbon monoxide liberation has mostly been studied on a macroscopic scale and at rather long irradiation times of several minutes. In this study we want to reveal the ultrafast primary processes of CO release and the incipient reactions involved. For this purpose, we employ time-resolved mid-infrared spectroscopy with different pump wavelengths, exposing an ultrafast dissociation process accompanied by the formation of new species. These experiments are complemented by linear spectroscopy methods and DFT calculations on the reactant as well as on a range of possible photoproducts.

MO 12.6 Tue 15:30 V38.03

Internal conversion vs. ultrafast intersystem crossing: A benchmark study on substituted cyclopenten-2-ones — ●OLIVER SCHALK^{1,2}, PETER LANG¹, GUORONG WU², MICHAEL S. SCHUURMAN², ALBERT STOLOW², and EBERHARD RIEDLE¹ — ¹BioMolekulare Optik, LMU, München — ²SIMS, Ottawa, Canada

Carbonyl groups are one of the most common functional groups in organic molecules. So far no systematic study exists to address their influence on excited state dynamics. Here we provide first insight using time-resolved photoelectron and transient absorption spectroscopy, as well as *ab initio* calculations to study the photodynamics of various substituted cyclopenten-2-ones in dependence on the solvent. We excite the molecules to the lowest $\pi\pi^*$ -state. Within 100 fs they reach an energetically lower $n\pi^*$ -state where the wavepacket bifurcates. Sev-

eral channels are open for a rapid return to the ground state, provided by conical intersections which are similar to those found in simple polyenes, including [1,2]-hydrogen migration, pyramidalization and ring opening [1]. However, experiments show that the vast majority of molecules instead perform intersystem crossing to the triplet manifold within 1-5 ps. A likely explanation for this behavior is a tilt in the conical intersection geometry induced by the carbonyl group which makes internal conversion hardly accessible for a change of potential energy surfaces. The rate for intersystem crossing is then determined by both, the relative energetic positions of the triplet and the $n\pi^*$ -state and spin orbit couplings which depend on solvent and substitution.

[1] O. Schalk et al., *J. Am. Chem. Soc.* **131**, 16451, (2011).

MO 12.7 Tue 15:45 V38.03

Time Resolved Photoelectron Photoion Coincidence Spectra of Sodium Doped Water Clusters — JAN P. MÜLLER^{1,2}, INGOLF V. HERTEL¹, and C.P. SCHULZ¹ — ¹Max Born Institute, Max-Born-Str. 2a, 12489 Berlin — ²Now at: TU Berlin, Institut für Optik und

Atomare Physik, Hardenbergstrasse 36, 10623 Berlin

Gas phase clusters of polar solvent molecules doped with an alkali metal atom are model systems for studying the behaviour of loosely bound metal valence electrons in a polar environment. In recent years, we have studied the lifetime of the first electronically excited state of sodium doped water clusters ($\text{Na}(\text{H}_2\text{O})_n$). It was found that the lifetime decreases rapidly with increasing cluster size down to about 100 fs for $n \geq 20$ [1]. These short lifetimes are presumably provoked by fast internal conversion, which is strongly correlated to the DOS of the intra molecular vibrations. Recently, we have performed time-resolved photoelectron photoion coincidence experiments. From the measured kinetic energy distributions of the electrons we gain more insight into the relaxation process. The results will be compared to similar measurements on negatively charged water clusters [2].

[1] H.T. Liu, J.P. Müller, N. Zhavoronkov, C.P. Schulz, I.V. Hertel, *J. Phys. Chem. A*, **114**, 1508 (2010).

[2] G.B. Griffin, R.M. Young, O.T. Ehrler, D.M. Neumark, *J. Chem. Phys.*, **131**, 194302 (2009).

MO 13: Poster 1: Cold Molecules, Femtosecond Spectroscopy, Molecular Dynamics

Time: Tuesday 16:30–19:00

Location: Poster.IV

MO 13.1 Tue 16:30 Poster.IV

Towards Cold Ion-Radical Chemistry with Magnetically Decelerated Atoms — KATRIN DULITZ¹, CHRIS J. RENNICK¹, MICHAEL MOTSCH², HANSJÜRGEN SCHMUTZ², FRÉDÉRIC MERKT², and TIMOTHY P. SOFTLEY¹ — ¹Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Mansfield Road, Oxford, OX1 3TA, United Kingdom — ²Laboratorium für Physikalische Chemie, ETH Zürich, CH-8093, Switzerland

Zeeman deceleration is an experimental technique in which inhomogeneous, pulsed magnetic fields are used to control the velocity of a supersonic beam. The method is based on the Zeeman interaction between paramagnetic particles and magnetic fields, enabling the deceleration of species like atomic hydrogen or molecular oxygen [1, 2]. We present the design of a 12-stage Zeeman decelerator for hydrogen atoms that can readily be integrated into an existing ion-trap setup [3] using a bent magnetic hexapole guide. This combined Zeeman decelerator - ion trap experiment will allow for experiments on cold ion-radical reactions, e. g., between H atoms and sympathetically cooled CO_2^+ . An extended version of the decelerator will be used for the deceleration of deuterium atoms to study kinetic isotope effects in low-temperature ion-radical reactions. The work will contribute towards the understanding of chemical reactivity in the low-temperature regime and it will provide fundamental tests for chemical reaction theories.

[1] N. Vanhaecke et al., *Phys. Rev. A* **75**, 031402 (2007). [2] E. Narvicius et al., *Phys. Rev. A* **77**, 051401 (2008). [3] S. Willitsch et al., *Phys. Rev. Lett.* **100**, 043203 (2008).

MO 13.2 Tue 16:30 Poster.IV

A centrifuge decelerator for supersonic beams of buffer-gas cooled polar molecules — ANDREAS ROHLFES, XING WU, CHRISTIAN SOMMER, SOTIR CHERVENKOV, MARTIN ZEPPENFELD, LAURENS VAN BUUREN, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, D-85748 Garching, Germany

We present a novel and versatile scheme for the production of quasi continuous beams of slow and internally cold polar molecules. We produce internally cold polar molecules by a supersonic expansion from a cryogenic buffer-gas cell, which results in the formation of a continuous and hydrodynamically enhanced beam of longitudinally fast molecules with a narrow velocity distribution. Further, these beams are accepted and guided by a quadrupole electric guide [1] to a centrifuge decelerator. The latter employs the centrifugal potential in a rotating frame to slow down the molecules when they are guided from the periphery to the center. With this deceleration scheme quasi continuous beams of internally cold and slow molecules with longitudinal velocities below 20m/s can be produced. Thus this technique is a suitable source of polar molecules for further experiments, e.g., trapping and subsequent opto-electrical cooling[2].

[1] L.D. van Buuren et al., *Phys. Rev. Lett.* **102**, 033001 (2009)

[2] M.Zeppenfeld et al., *Phys. Rev. A* **80**,041401(R) (2009)

MO 13.3 Tue 16:30 Poster.IV

Reaching for the Ultracold with Polyatomic Molecules —

BARBARA G.U. ENGLERT, ROSA GLÖCKNER, ALEXANDER PREHN, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

Realizing a general method for cooling polar molecules to ultracold temperatures has been a key area of research over the past decade. The precise control over the molecular degrees of freedom possible at ultracold temperatures combined with the strong dipole-dipole interaction makes ultracold molecules attractive candidates for applications reaching from many-body physics to quantum information science. A highly versatile technique to cool a large variety of polyatomic molecules to the microkelvin regime is opto-electrical cooling [1]. In this general Sisyphus-type cooling scheme the strong interaction of polar molecules with electric fields is exploited to repeatedly remove a large amount of kinetic energy in a single step.

Here we present the first experimental realization of opto-electrical cooling using trapped CH_3F . Trapping is achieved with a microstructured electric trap [1,2] providing a record-long lifetime of over 10 s. Vibrational and rotational molecular states are driven using infrared and microwave fields, with homogeneous electric fields in the trap allowing selective addressing of rotational M-sublevels. We achieve a reduction of the molecular temperature from 358 mK to 77 mK, and an increase of the phase-space density by a factor of 7.

[1] M. Zeppenfeld et al., *Phys. Rev. A* **80**, 041401(R) (2009).

[2] B.G.U. Englert et al., *Phys. Rev. Lett.*, in press (arXiv:1107.2821).

MO 13.4 Tue 16:30 Poster.IV

Laboratory Astrochemistry in a Multipole RF Ion Trap —

THORSTEN BEST¹, ERIC ENDRES¹, RICO OTTO^{1,2}, and ROLAND WESTER¹ — ¹Inst. f. Ionenphysik u. Angew. Physik, Universität Innsbruck — ²now at Dept. of Chemistry, Univ. of California San Diego

Multipole radio-frequency ion traps provide a favourable environment for laboratory astrochemistry. Collisional cooling with a neutral buffer gas allows to reach the temperature range characteristic for e.g. the interstellar medium, in both the internal and motional degrees of freedom, and to store molecular ions for extended periods of time.

Through coupling of a 22-pole ion trap with a high resolution time of flight mass spectrometer, sensitive measurements of both collision-induced (e.g. reactive) and radiation-induced processes become feasible. We demonstrate the applicability of this experimental setup to several problems in laboratory astrochemistry, including photodetachment [1] and reactions with H_2 .

A new perspective for the detection and analysis of gas phase molecules and clusters has recently been opened by the development of novel radiation sources in the Terahertz domain. In combination with powerful astronomical observation tools such as HERSCHEL and ALMA, laboratory THz spectroscopy may lead to the discovery of new species in various astronomical environments. We present our approach towards THz action spectroscopy on cold trapped molecular

ions.

[1] T. Best et al., *Ap.J.* 742, 63 (2011)

MO 13.5 Tue 16:30 Poster.IV

Detection of Li atoms scattered from a magneto-optical trap by using slow and cold molecular beams — ●BERNHARD RUFF, MATTHIAS STREBEL, MARCEL MUDRICH, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Herman-Herder-Str. 3, D-79104 Freiburg im Breisgau

Slow beams of cold molecules or atoms produced by a rotating nozzle are scattered with magneto-optically trapped Li atoms. Detection of Li by means of surface ionization on a hot ribbon allows to observe elastic and inelastic scattering processes as a function of kinetic energy down to about 1 meV. Technical details regarding the slow molecular beam source, the ultra-cold scattering target and the detection schemes are discussed. Furthermore, first measurements with different atomic and molecular beams are presented.

MO 13.6 Tue 16:30 Poster.IV

Cold molecular collisions with merged beams — ●ANA ISABEL GONZALEZ FLOREZ¹, JANNEKE BLOKLAND¹, HENRIK HAAK¹, NICOLAS VANHAECKE¹, SEBASTIAAN Y T VAN DE MEERAKKER², and GERARD MEIJER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Radboud University Nijmegen, Nijmegen, the Netherlands

Beams of Stark-decelerated molecules have proven to be versatile in studying collisions between atoms and molecules at low collision energies. In these crossed-beam experiments the minimal collision energy was limited to 50 cm⁻¹ by the center-of-mass kinetic energy of the atoms (50 cm⁻¹), hampering the observation of resonances in the scattering cross-section that are predicted to occur at lower energies.

Currently we are developing a set up to collide merged beams of atoms and Stark-decelerated molecules to reach collision energies down to 5 cm⁻¹. We use a curved hexapole to guide Stark-decelerated molecules, such as metastable CO or ND₃, in order to merge them with a beam of He atoms. The He atoms are injected through vacuum with an Even-Lavie valve and cooled down with a cold head. The relative velocity between the two beams can be varied by changing the final velocity of the Stark-decelerated molecules, thus changing the collision energy. Finally, the molecules can be state-selectively detected using (1+1) or (2+1) REMPI, in case of CO or ND₃ respectively.

MO 13.7 Tue 16:30 Poster.IV

Towards precision spectroscopy of laser cooled molecules — ●CORINE MEINEMA, JOOST VAN DEN BERG, KLAUS JUNGSMANN, AERNOUT VAN DER POEL, and STEVEN HOEKSTRA — KVI, University of Groningen, The Netherlands

We aim to use lasercooling to bring alkaline-earth monohalide molecules to ultracold temperatures, in order to perform high-precision spectroscopic tests of fundamental physics. The selected group of molecules is promising because an (almost) closed cycle for lasercooling can be created using a limited number of lasers. By using a Stark decelerator to reduce the average speed of a molecular sample, the required number of scattered photons to reach the ultracold regime (*sim* 100 μK) is greatly reduced. We are currently working on a supersonic beam of SrF molecules, constructing a Stark-decelerator based on ring electrodes, and setting up the required lasers. Especially interesting to us are the challenges and possibilities of lasercooling molecules in the presence of electric fields. A new generation of precision measurements to probe fundamental interactions and symmetries is possible once such samples of sufficiently cold molecules are available.

MO 13.8 Tue 16:30 Poster.IV

A Molecular Laboratory on a Chip — ●MARK ABEL, SILVIO MARX, SAM MEEK, ANNA ISABEL GONZALEZ FLOREZ, GABRIELE SANTAMBROGIO, and GERARD MEIJER — Fritz-Haber Institut der MPG, 4-6 Faradayweg, 14195 Berlin, Germany

In the past several years, Stark deceleration has proved to be a powerful tool for controlling the translational motion of neutral polar molecules. Chip-based Stark decelerators offer many advantages over the macroscopic designs used previously; among these are relatively low voltage requirements, high field gradients, and tight spatial confinement of polar molecules. In addition, chip-based decelerators offer good optical access for spectroscopic probing and control of the trapped molecules. We show the design of our "molecular lab on a chip," its performance,

and the results of rotational- and vibrational spectroscopy on trapped molecules.

MO 13.9 Tue 16:30 Poster.IV

Low energy scattering of Stark-decelerated OH radicals with He atoms with high energy resolution — ●H. CHRISTIAN SCHEWE¹, MORITZ KIRSTE¹, XINGAN WANG¹, LUDWIG SCHARFENBERG¹, NICOLAS VANHAECKE¹, SEBASTIAAN Y.T. VAN DE MEERAKKER², and GERARD MEIJER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²Radboud University Nijmegen, Institute for Molecules and Materials, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

For collision studies of molecules, a Stark decelerator offers the advantage that it produces beams of cold neutral polar molecules with a tunable velocity. A second beam of atoms or molecules will be crossed to study scattering down to collision energies of a few wavenumbers.

We present future experiments where in particular the inelastic scattering of Stark-decelerated and state-selected OH(X ²Π_{3/2}, J = 3/2,f) with helium atoms will be carried out [1]. To reach low collision energies down to 10 cm⁻¹ a pulsed valve of the Even-Lavie type is mounted on a helium cryostat. The translational velocity and the speed ratio of Helium beams are characterized and their dependence on the temperature, the stagnation pressure and the opening time of the valve are determined. Simulations are presented to show how the resolution of the collision energy can be optimized by bunching of the molecular packet inside the decelerator. We give a perspective on how theoretically predicted scattering resonances of the inelastic cross section might be resolved.

[1] Kirste et al. *Phys. Rev. A* 82, 4 (2010).

MO 13.10 Tue 16:30 Poster.IV

Systematic analysis of long-range interactions between vibrating polar alkali molecules — ROMAIN VEXIAU, MAXENCE LEPERS, MIREILLE AYMAR, ●OLIVIER DULIEU, and NADIA BOULOUFA — laboratoire Aimé Cotton, CNRS, Université Paris-Sud, Orsay, France

The determination of the long-range anisotropic interactions between polar alkali molecules is of crucial importance for the achievement of a quantum gas of ultracold polar molecules. In particular, the dispersion coefficient C₆ of the van der Waals interaction depends on the dynamic polarizability of the molecule evaluated at imaginary frequencies, expressed as a sum over all possible radiative transitions of electronic dipole moments. Using a mixture of up-to-date spectroscopic data and accurate ab initio data for potential energy curves, and permanent and transition dipole moments, we have obtained the values of the dispersion coefficients between identical polar molecules (LiNa, LiK, LiRb, LiCs, NaK, NaRb, NaCs, KRb, KCs, RbCs) in an arbitrary vibrational level of their electronic ground state. A careful analysis of the importance of the various kinds of transitions contributing to the sum has been performed. The C₆ values significantly decrease with increasing vibrational levels towards the sum of the C₆ coefficients between the four involved atomic pairs. For the lowest vibrational levels the C₆ parameter varies from about 10⁴ atomic units for KRb up to 10⁷ atomic units for NaCs, which will lead to different collisional regimes at ultracold temperatures.

MO 13.11 Tue 16:30 Poster.IV

High-resolution LIR-spectroscopy of molecular ions — ●OSKAR ASVANY, SANDRA BRÜNKEN, LARS KLUGE, SABRINA GÄRTNER, and STEPHAN SCHLEMMER — I. Physikalisches Institut, Universität zu Köln

Laser Induced Reaction (LIR) is a powerful technique for the spectroscopy of molecular ions as well as the study of state-specific rate coefficients. It is based on trapping mass-selected ions in a cryogenic ion trap and probing their laser-induced excitation by the outcome of an endothermic ion-molecule reaction. In particular, the combination of cold ions with a narrow-bandwidth optical parametric oscillator (OPO) enables highly accurate determination of rovibrational transitions. In this poster, the application of this technique to H₃⁺, CH₂D⁺ and CH₅⁺ in the 3 micron wavelength region is presented. H₃⁺ and CH₂D⁺ are molecules of mostly astrophysical interest. For CH₂D⁺, the presented method yielded rovibrational lines known with MHz accuracy. A standard asymmetric rotor model fitted to the data transferred this accuracy to the ground state rotational transitions. The method demonstrated here could be a useful way to determine rotational transitions which are difficult to measure in the microwave region. The ion CH₅⁺ is known to be the prototype of a floppy molecule. For this reason, its chaotic

spectrum presented by Takeshi Oka in 1999 is still unexplained. Applying the LIR-technique, the prospects of obtaining high-resolution information of CH_5^+ are discussed. In this particular case, cooling of this floppy ion to populate only the lowest states will be crucial for the feasibility of the experiment.

MO 13.12 Tue 16:30 Poster.IV

Ultrafast Circular Dichroism Investigation of the Ring Opening in 7-Dehydrocholesterol — ●JULIA MEYER-ILSE^{1,2}, DENIS AKIMOV², and BENJAMIN DIETZEK^{1,2} — ¹Institute of Physical Chemistry and Abbe Center of Photonics, Friedrich-Schiller University Jena, Jena, Germany — ²Institute of Photonic Technologies (IPHT) Jena e.V., Jena, Germany

UV-femtosecond time-resolved circular dichroism (TRCD) spectroscopy has been used to study the ultrafast changes of chirality in a small molecular biological paradigm sample, 7-dehydrocholesterol (7-DHC). Upon UV-photoexcitation, 7-DHC undergoes a ring opening to produce previtamin D3 and two of the chiral centers of 7-DHC are removed, which impacts the overall chirality of the molecule. Here, measurements of this chirality change connected to the ring opening of 7-DHC with a time-resolution of 280 fs are reported. With this method a previously described discrepancy concerning the photophysics of 7-DHC was clarified. With our set-up the relaxation time of the chirality change was measured to be 1-2 ps, which corresponds to the shortest time-constant in the transient absorption (TA) measurements, allowing us to assign that time-constant to the ring opening.

MO 13.13 Tue 16:30 Poster.IV

Femtosecond Coherence Spectroscopic Study of the Onset of Chemical Denaturation of Myoglobin upon Addition of Minor Amounts of Urea — ●JULIA MEYER-ILSE^{1,2}, DENIS AKIMOV², and BENJAMIN DIETZEK^{1,2} — ¹Institute of Physical Chemistry and Abbe Center of Photonics, Friedrich-Schiller University Jena, Jena, Germany — ²Institute of Photonic Technologies (IPHT) Jena e.V., Jena, Germany

The interaction of urea with myoglobin, as a benchmark system for heme-containing proteins, is studied via femtosecond coherence spectroscopy. The work focuses on the effect of urea on the appearance of low-wavenumber oscillations, which are a measure of the geometrical structure of the heme group and its interaction with the polypeptide chain. Pursuing this approach, structural alterations (i.e. changes in the vibrational dynamics of the heme group) are detected at denaturant concentrations below the full denaturation limit of 6M urea for myoglobin. In particular, the low-wavenumber oscillation associated with the heme-doming (i.e. the out-of-plane vibration of the porphyrin macrocycle) is found to appear spectrally shifted with a concentration of only 3M urea. These results suggest that the local environment around the heme is already altered despite the fact that macroscopic unfolding as manifested in the thermodynamic properties of the polypeptide chain is not complete at these urea concentrations.

MO 13.14 Tue 16:30 Poster.IV

Investigations on the Circular Dichroism in the Photoelectron Angular Distributions of Camphor and Fenchone using circularly polarized femtosecond UV-laser pulses — CHRISTIAN LUX, ●VANESSA BRANDENSTEIN, TOM BOLZE, CRISTIAN SARPE, MATTHIAS WOLLENHAUPT, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSaT, D-34132 Kassel, Germany

Enantiomers of a chiral molecule that are non super imposable mirror images of each other show almost the same physical properties. In the recent past experiments on enantiomers based on laser irradiation using circularly polarized ultrashort laser pulses [1,2] or synchrotron radiation [3] were realized for chiral molecules.

In this contribution we investigate the effect of Circular Dichroism on the Photoelectron Angular Distributions (PECD) in the Resonance Enhanced Multi-Photon Ionization of Camphor and Fenchone employing femtosecond ultraviolet-laser pulses [4]. Our experiments have been extended to studies of the Above Threshold Ionization and dependencies of the PECD on parameters like intensity, chirp and ellipticity.

[1] C. Logé, A. Bornschlegel, U. Boesl, *Anal. Bioanal. Chem.* **395**, 1631-1639 (2009)

[2] P. Horsch, G. Urbasch, K.-M. Weitzel, *Z. Phys. Chem.* **225**, 587-594 (2011)

[3] I. Powis in S. A. Rice (Ed.): *Adv. Chem. Phys.* **138**, 267-329 (2008)

[4] C. Lux, M. Wollenhaupt, T. Bolze, Q. Liang, C. Sarpe, T. Baumert (*in preparation*) (2011)

MO 13.15 Tue 16:30 Poster.IV

Accessing higher-lying Reaction Pathways of a Molecular Switch by Femtosecond Pump-Repump-Probe Spectroscopy — ●STEFAN RUETZEL, MARTIN KULLMANN, JOHANNES BUBACK, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Many photochromic compounds and their ultrafast dynamics after photoexcitation have been studied in recent years by means of femtosecond spectroscopy such as transient absorption measurements. However, the role of higher-lying excited states in these photoreactions has not been explored for many of these systems. By exploiting spectrally resolved pump-repump-probe transient absorption spectroscopy we are able to resolve the kinetics that happen after excitation to higher-lying electronic states.

Here we present pump-repump-probe data of the molecular switch 6,8-dinitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline], a photochromic system present in two ring-open isomers in solution which differ in a cis/trans configuration of a double bond. The pump pulse excites the molecule to its first electronically excited state, the second pulse is resonant with excited-state absorption, and the whitelight probe pulse allows the observation of many possible product absorptions. Our data suggests the formation of new absorbing species triggered by optical repumping of the main isomer. A detailed data analysis as well as a discussion of possible photoproducts to be formed after repumping is presented.

MO 13.16 Tue 16:30 Poster.IV

Fragment momentum distributions obtained from coupled electron-nuclear dynamics — ●KILIAN HADER and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg

We theoretically investigate fragmentation processes induced by femtosecond laser pulses within a model which incorporates electronic and nuclear motion. Single-pulse excitation leads to diffraction patterns in the electron-momentum distribution which depend on the nature of the electronic state and also on the nuclear charge distribution. Additional structures appear in the nuclear-momentum distribution if two time-delayed pulses produce fragments in the same dissociation channel. It is shown that these functions are modified by the electronic degree-of-freedom. A simultaneous excitation of two different electronic state results in further interferences which are related to electronic wavepacket dynamics on the attosecond time-scale.

MO 13.17 Tue 16:30 Poster.IV

Ionisation von H_2^+ in starken Laserfeldern — ●KEVIN PAHL, MAX SCHÜTT, MATTHIAS ODENWELLER, LOTHAR SCHMIDT, MAKSIM KUNITSKI, JIAN WU, JASMIN TITZE, MARKUS WAITZ, DANIEL METZ, CHRISTOPH GOIHL, FLORIAN TRINTER, JÖRG VOIGTSBERGER, CHRISTIAN MÜLLER, TILO HAVERMEIER, HENDRIK SANN, HORST SCHMIDT-BÖCKING und REINHARD DÖRNER — Institut für Kernphysik, Farnkfurt a.M.

Untersuchung der Ionisation von H_2^+ in starken Laserfeldern. Die Moleküle werden durch Stoßionisation ionisiert und in einem Teilchenbeschleuniger beschleunigt. Der Ionenstrahl wird anschließend mit einem Femtosekundenlaser, der Wellenlänge von 400nm, mit einer Leistung von $5 \cdot 10^{14} \text{W/cm}^2$ im Fokus, zum Überlapp gebracht. Dabei können alle bei der Ionisation freiwerdenden Ionen und Elektronen gemessen werden. Durch eine Messung der 2-dimensionalen Ortsprojektion der Reaktionsprodukte und der Flugzeit, kann die Reaktion im 3-dimensionalen Impulsraum vollständig rekonstruiert und analysiert werden. Darüber hinaus ermöglicht dies eine Berechnung der Reaktionsenergien und Darstellung der jeweiligen Winkelverteilung.

MO 13.18 Tue 16:30 Poster.IV

Ionisation von NH_2^+ in starken Laserfeldern — ●MAX SCHÜTT, KEVIN PAHL, MATTHIAS ODENWELLER, LOTHAR SCHMIDT, MAKSIM KUNITSKI, JIAN WU, JASMIN TITZE, MARKUS WAITZ, DANIEL METZ, CHRISTOPH GOIHL, FLORIAN TRINTER, JÖRG VOIGTSBERGER, CHRISTIAN MÜLLER, TILO HAVERMEIER, HENDRIK SANN, HORST SCHMIDT-BÖCKING und REINHARD DÖRNER — Goethe-Universität Frankfurt am Main

Untersuchung der Ionisation von NH_2^+ in starken Laserfeldern. Die Moleküle werden durch Stoßionisation ionisiert und in einem Teilchenbeschleuniger beschleunigt. Der Ionenstrahl wird anschließend mit einem Femtosekundenlaser mit einer Leistung $5 \cdot 10^{14} \text{W/cm}^2$ im Fo-

cus und einer Wellenlänge von 400nm, zum Überlapp gebracht. Dabei können alle bei der Ionisation freiwerdenden Ionen und Elektronen gemessen werden. Durch eine Erfassung der 2-dimensionalen Ortsprojektion der Reaktionsprodukte und der Flugzeit, kann die Reaktion im 3-dimensionalen Impulsraum vollständig rekonstruiert und analysiert werden. Darüber hinaus ermöglicht dies eine Berechnung der Reaktionsenergien und Darstellung der jeweiligen Winkelverteilung.

MO 13.19 Tue 16:30 Poster.IV

Controlling large molecules at kHz repetition rates — SEBASTIAN TRIPPEL¹, TERENCE G. MULLINS¹, NELE MÜLLER¹, KAROL DŁUGOLECKI¹, and JOCHEN KÜPPER^{1,2} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²University of Hamburg

With our new experimental setup we aim for studying ultrafast dynamics of large and complex molecules directly in the molecular frame. In first benchmark experiments we create supersonic, cold beams of prototypical iodobenzene (C₆H₅I) molecules at high repetition rates – up to 1 kHz. These molecular beams are quantum-state selected by dc electric fields [1,2] and, subsequently, laser aligned and mixed-field oriented by strong picosecond laser fields and weak dc electric fields [2]. The resulting strongly aligned and oriented molecular samples are characterized by strong-field ionization using femtosecond laser pulses and velocity-map imaging of the produced ions to derive the angular distribution of the molecules. The degrees of alignment and orientation are characterized as a function of repetition rate, state selection, and laser parameters. In the future, the high repetition rate will allow us to investigate weak processes in molecular dynamics, exploiting, for instance, molecular-frame photoelectron angular distributions [3].

- [1] F. Filsinger et al., *Angew. Chem. Int. Ed.*, **48**, 6900-6902 (2009)
- [2] L. Holmegaard et al., *Phys. Rev. Lett.*, **102**, 023001 (2009)
- [3] L. Holmegaard et al., *Nature Physics*, **6**, 428 (2010)

MO 13.20 Tue 16:30 Poster.IV

Femtosecond Time-Resolved Transient Grating Spectroscopy for the Investigation of Exciton Dynamics in Thin Films of PTCDA — TAHIR ZEB KHAN, KHADGA J. KARKI, MAHESH NAMBOODIRI, and ARNULF MATERNY — Research Center for Functional Materials and Nanomolecular Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany

Elementary processes like energy transfer, charge transport, and exciton diffusion in thin films occur on time scales of femtoseconds. Time-resolved photoelectron spectroscopy, a technique limited to specialized ultra-high vacuum environment and the proper choice of substrate, has been used to study ultrafast processes in sub-nanometer thin films so far. In our contribution, we show that a transient (population) grating created by the interference of femtosecond laser pulses can be applied successfully to access ultrafast processes in such films under ambient conditions. Our investigations of exciton dynamics in 1.4 ± 0.2 and 0.4 ± 0.2 nm thin films, formed by nano crystals of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) on glass and mica, show that the dynamics differ with the crystal size, possibly due to the confinement-induced changes in the electronic structure. The technique is sensitive enough to investigate the dynamics in systems, where only 20% of the surface is covered by nano crystals. This is an important prerequisite for studying ultrafast dynamics on surfaces, interfaces, functionalized materials, organic semiconductors, and quantum phenomena in ordered structures of reduced dimensions, such as quantum dots and graphene sheets.

MO 13.21 Tue 16:30 Poster.IV

Photoinduced Processes in a Low-Spin Cobalt(II) Semiquinonate Complex — FABIAN RUPP¹, KATHARINA CHEVALIER¹, MATTHIAS M.N. WOLF¹, MICHELE GRAF², HARALD KELM², HANS-JÖRG KRÜGER², and ROLF DILLER¹ — ¹Dept. of Physics, Univ. Kaiserslautern — ²Dept. of Chemistry, Univ. Kaiserslautern, 67663 Kaiserslautern, Germany

Metal complexes undergoing valence tautomerism and spin-crossover by external stimuli may be utilized as novel molecular switches [1]. Here we study ultrafast photoinduced processes in the first cobalt(II) semiquinonate complex, that displays spin-crossover properties rather than valence tautomerism [2], by means of femtosecond time-resolved pump-probe-spectroscopy in solution. After photoexcitation of [Co(L-N₄tBu₂)(dbsq)](B(p-C₆H₄Cl)₄) we probe in the visible/near-infrared (IR) and mid-IR range for dynamical and structural information on the transient species [3]. The observed kinetics support the parallel formation of two cobalt(III) catecholate species with different spin multiplicity that replenish the ground state on a picosecond time scale.

The model will be advanced by quantum chemical calculations and further time-resolved as well as steady-state studies of similar complexes that may allow to identify vibrational marker bands for the assignment of possible redox- and spin-states.

- [1] J.-F. Letard et al., *Top. Curr. Chem.* **235**, 221 (2004)
- [2] M. Graf et al., *Angew. Chem., Int. Ed.* **49**, 950 (2010)
- [3] M.M.N. Wolf et al., *Phys. Chem. Chem. Phys.* **10**, 4264 (2008)

MO 13.22 Tue 16:30 Poster.IV

Efficient and robust strong-field control of population transfer in sensitizer dyes with designed femtosecond laser pulses — JOHANNES SCHNEIDER, MATTHIAS WOLLENHAUPT, ANDREAS WINZENBURG, TOBIAS BLUMENSTEIN, TIM BAYER, JENS KÖHLER, RÜDIGER FAUST, and THOMAS BAUMERT — University of Kassel, Institute of Physics and CINSaT, D-34132 Kassel, Germany

We demonstrate control of electronic population transfer in molecules with the help of shaped femtosecond laser pulses. To that end we investigate two photosensitizer dyes in solution being prepared in the triplet ground state. Excitation within the triplet system is followed by intersystem crossing and the corresponding singlet fluorescence is monitored as a measure of population transfer in the triplet system. We record control landscapes with respect to the fluorescence intensity on both dyes by a systematic variation of laser pulse shapes combining second order and third order dispersion. In the strong-field regime we find highly structured topologies with large areas of maximum or minimum population transfer being robust with respect to the applied laser intensities. We then compare our experimental results with simulations on generic molecular potentials by solving the TDSE for excitation with shaped pulses. The analysis of the regions of maximum or minimum population transfer reveals that coherent processes control the outcome of the excitation process. Within this context we give an outlook on the application of strong field controlled fluorescence to nonlinear microscopy.

MO 13.23 Tue 16:30 Poster.IV

Investigation of vibrational coherence generation by femtosecond two-pulse excitation experiments — JAN PHILIP KRAACK, MARCUS MOTZKUS, and TIAGO BUCKUP — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

Vibrational coherences in nonlinear optical spectroscopy are prepared by two distinct light-matter interactions. These may take place within the temporal envelope of a single excitation pulse of femtosecond time duration in, e.g., two-pulse pump-probe spectroscopy. Alternatively, each interaction may take place within the temporal envelope of independent excitation pulses as in, e.g., three-pulse Degenerate Four-Wave-Mixing (DFWM)[1]. The application of two distinct excitation pulses in DFWM offers important advantages over single excitation pulse techniques regarding investigations of electronic coherence dynamics. We experimentally and theoretically investigated effects of variable interpulse delays between excitation pulses in spectrally-resolved and -integrated DFWM. Clear oscillatory modulation of normal mode signal intensities is observed for a series of samples with different vibrational characteristics when the interpulse delay is scanned. These modulation effects are strongly dependent on the displacements between involved electronic states as well as the number of involved vibrational modes.

- [1]Kraack, J. P.; Motzkus, M.; Buckup, T. *The Journal of Chemical Physics* 2011, 135, 224505.

MO 13.24 Tue 16:30 Poster.IV

CRASY: Correlated Rotational Alignment Spectroscopy of Molecules and Clusters — CHRISTIAN SCHRÖTER and THOMAS SCHULTZ — Max-Born-Institut, Berlin

When a molecule is ionized, the formed electron and ion can be detected with quantum yields close to one, leading to an extraordinarily sensitive characterization of molecular mass and electronic structure. By using pump-probe ionization schemes, the characterization can be extended to photoexcited species to observe photochemical reactions in real time. The information content of such experiments, however, is insufficient for spectroscopic assignment of molecular structure in all but the most trivial molecules.

Rotational spectroscopy is a very sensitive tool to characterize molecular structure. We recently demonstrated the correlated measurement of rotational spectra and pump-probe ionization spectra by correlated rotational alignment spectroscopy (SCIENCE 333, 1011 (2011)).The experiment combines the extraordinary sensitivity of ion-

ization spectroscopy with the high-resolution information of rotational spectroscopy. Through the simultaneous determination of molecular masses, electron binding energies, and rotational structure for multiple species in a sample, CRASY can generate spectroscopic data of a new quality and with unprecedented information content. Our poster will present the experimental technique and show recent results of CRASY measurements.

MO 13.25 Tue 16:30 Poster.IV

High Harmonic Spectroscopy of NO₂: Electronic Dynamics and Molecular Dissociation — ●CHUNG-HSIN YANG¹, CHRISTIAN NEIDEL¹, JESSE KLEI¹, ARJAN GIJSBERTSEN³, MARC VRAKKING¹, and HANS JAKOB WÖRNER² — ¹Max-Born-Institut, Berlin — ²ETH, Zürich — ³AMOLF, Amsterdam

Time-resolved photoelectron and photoion velocity map imaging (VMI) experiments have been used to study NO₂ excited close to its first dissociation limit, leading to NO (XII) and O (3P) fragments. The NO₂ molecule was excited to its A ²B₂ excited electronic state by one pump photon at a center wavelength of 395 nm, followed by a probe laser pulse in the XUV wavelength region from a high-harmonics source. The first excited electronic state of NO₂, A ²B₂, is embedded within the X ²A₁ electronic ground state and is strongly coupled to the X ²A₁ state via a conical intersection between the two potential energy surfaces. By varying the time delay between the pump and probe lasers, we probe the photodynamics of NO₂ by measuring photoion and photoelectron momentum distributions. In our measurements, both NO⁺ and O⁺ yields show exponential growth (1-1.5ps rise time) corresponding to the dissociation time scale observed from previous energy dependence studies. For the photoelectron results, some channels with hundred femtoseconds or picoseconds dynamics have been ascribed to the ionization of NO₂ molecule in X ²A₁ or A ²B₂ state, or fragments. However, contributions from electrons correlating with different ions and produced by different high harmonics result in a large complexity of photoelectron images.

MO 13.26 Tue 16:30 Poster.IV

Time-resolved photoelectron imaging of excited state dynamics in nitric oxide (NO) in the VUV range — PETER TRABS, FRANZISKA BUCHNER, ●ANDREA LÜBCKE, ARNAUD ROUZÉE, HANS-HERMANN RITZE, MASOOD GHOTBI, and MARC VRAKKING — Max-Born Institut Berlin

40 fs tuneable VUV pulses in the range of 147 nm - 150 nm are used to trigger electron dynamics in Rydberg states of NO. A second delayed pulse at 800 nm probes the excited state by photoionization. A velocity map imaging spectrometer is used to measure the angular and kinetic energy distribution of the ejected photoelectrons in dependence of the delay between pump and probe pulses. We observe three photoelectron lines and find different oscillations in the photoelectron yield, the kinetic energy and the angular distribution. These results are interpreted in terms of beating between different vibronic states.

MO 13.27 Tue 16:30 Poster.IV

The test of approximate relation between inter-nuclear distances and vibration frequencies in a few-atomic molecule — ●VLADIMIR DAMLJANOVIC — Institute of Physics Belgrade, Pregrevica 118, 11080 Belgrade, Serbia

Recently, the author has found a group of coordinate transformations that are symmetries of the electronic effective potential and the potential seen by nuclei in a molecule subjected to no external fields [arXiv:1111.4788v1]. In the lowest order approximation for the electronic effective potential adapted to these symmetries, one obtains the approximate relation between the equilibrium distances among nuclei in the molecule and its vibration frequencies. In this contribution we have tested this approximation for a variety of simple molecules.

MO 13.28 Tue 16:30 Poster.IV

Multidimensional Quantum Dynamics of Coupled Carbonyl Vibrations — ●MATEUSZ LISAJ and OLIVER KÜHN — Institute of Physics, Rostock University, Rostock, Germany

The six coupled carbonyl vibrations in the model system Fe₂(μSC₃H₆ - S)(CO₆) are investigated. First, quantum chemical (DFT) calculations are performed to span a six-dimensional potential energy surface (PES) in terms of normal mode coordinates. Relevant anharmonic couplings are identified and strategies for representation of PES and dipole moment surface are derived. The quantum dynamics of this model system is studied on the basis of the Multiconfiguration

time-dependent Hartree method. Emphasis is put on the signatures of anharmonic couplings in linear and nonlinear infrared spectroscopy.

MO 13.29 Tue 16:30 Poster.IV

Ultrafast Exciton Quenching upon Geometry Deformation in Molecular Aggregates — ●ALEXANDER SCHUBERT¹, VOLKER SETTELS¹, WEN-LAN LIU^{1,2}, FRANK WÜRTHNER¹, CHRISTOPH MEIER³, REINHOLD FINK^{1,4}, STEFAN SCHINDLBECK⁵, STEFAN LOCHBRUNNER⁶, BERND ENGELS¹, and VOLKER ENGEL¹ — ¹Universität Würzburg — ²Universität Heidelberg — ³Université de Toulouse — ⁴Universität Tübingen — ⁵LMU München — ⁶Universität Rostock

The efficiency of energy transport in molecular pi-aggregates is strongly attenuated by de-excitation mechanisms. We investigated experimentally and theoretically dimer aggregates of 3,4,9,10-perylene tetracarboxylic bisimide acid, exemplarily.

The measured absorption spectra could be interpreted assuming dipole-dipole coupling and a single effective vibrational monomer mode. An additional intermolecular torsional mode explained the fluorescence spectroscopic measurements indicating a long radiative lifetime and a low fluorescence yield. We now established an insight into the decay dynamics of optically excited state and the reaction path to the fluorescing state. Transient absorption measurements show that the excited state decays non-radiatively on an ultrafast fs-time-scale. This decay can be reproduced by a geometry change which increases the non-adiabatic transition effectivity. For that purpose we determined potential energy curves along a reaction coordinate relating the Franck-Condon geometry to a charge transfer configuration where the monomers exhibit the anion and cation geometry.

MO 13.30 Tue 16:30 Poster.IV

Non-adiabatic on-the-fly molecular dynamics on the formation of the DNA Dewar photolesion: Implementation of ONIOM and CASPT2 — ●SVEN OESTERLING, ARTUR NENOV, BENJAMIN P. FINGERHUT, and REGINA DE VIVIE-RIEDLE — Ludwig Maximilians Universität München, Department Chemie

Semiclassical on-the-fly dynamics provide a way to simulate molecular processes of moderate sized systems. Treating the nuclei classically, abolishes the need to precompute potential energy surfaces, and thus allows for a full dimensional treatment of the molecular degrees of freedom. The electronic properties are computed with quantum chemical methods, adequate for system-size and nature of the problem. This combination makes the whole approach an useful tool to investigate non-adiabatic reactions in many biologically relevant molecules, such as the nucleobases.

In the process of describing the formation and reversion of the DNA Dewar photolesion, we implemented an interface for the Molpro quantum chemistry package, in the Newton-X dynamics package. The two main features are the complete active space perturbation theory (CASPT2) and a hierarchical layer scheme (ONIOM). While CASPT2 yields very precise results for the electronically excited bases, the ONIOM method enables embedding the photoactive fragments into the phosphate-desoxyribose backbone, treated with computationally less demanding ground-state methods. In this way both, photochemical, as well as sterical effects can be accounted for, in an appropriate fashion.

MO 13.31 Tue 16:30 Poster.IV

Rotational effects on enantioseparation — ●ANDREAS JACOB and KLAUS HORNBERGER — Universität Duisburg-Essen, Fakultät für Physik, Lotharstraße 1-21, 47057 Duisburg

Recently, several ideas to separate enantiomers have been proposed, i.e. to split molecules in a left handed configuration from their right handed mirror state [1,2]. They are based on the dynamics caused by the equations of motion in an adiabatic basis produced by laser induced gauge potentials. Since the effect of molecular rotation has been neglected in these studies, we study the influence of the orientation state on the enantioseparation by numerical integration of the full molecular rotation state. We find that the potential from the adiabatic dressed state approach cannot be recovered, even in the rotational ground state. The obtained time-averaged interaction potentials and the associated forces are then strongly diminished, but they can still exhibit chiral sensitivity.

[1] Li, Bruder and Sun, Physical Review Letters 99, 130403 (2007)

[2] Li and Shapiro, The Journal of Chemical Physics 132, 194315 (2010)

MO 14: Poster 2: Biomolecules, Electronic Spectroscopy, Experimental Techniques, Quantum Chemistry, Various Topics

Time: Wednesday 16:30–19:00

Location: Poster.IV

MO 14.1 Wed 16:30 Poster.IV

Intensity Fluctuations of the Fluorescence of Individual Pigment-Protein Complexes from *Rhodospseudomonas acidophila*. — ●SEBASTIAN R. BEYER¹, MARIO SCHÖRNER¹, ALEXANDER LÖHNER¹, JUNE SOUTHALL², RICHARD J. COGDELL², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — ²Institute of Molecular, Cell and Systems Biology, College of Medical, Veterinary and Life Sciences, Biomedical Research Building, Glasgow G12 8QQ, Scotland, UK

The photosynthetic apparatus of purple bacteria is a highly efficient system to convert solar radiation into biological usable forms of energy. Part of this photosynthetic apparatus are the so called pigment-protein complexes. These membrane proteins are responsible for the initial step in the photosynthesis of purple bacteria – the absorption of sunlight.

We present a study on the temporal evolution of fluorescence emission from single pigment-protein complexes. Light harvesting complexes from purple bacteria were investigated under controlled environmental conditions with respect to their fluorescence intensity as well as their spectral properties as a function of time.

MO 14.2 Wed 16:30 Poster.IV

Label-free and quantitative mapping of nucleic acids in cells and tissues — ●PAOLA PIREDDA, VENKATNARAYAN RAMANATHAN, GREGOR HEHL, and ANDREAS VOLKMER — 3rd Institute of Physics, University of Stuttgart, 57 Pfaffenwaldring 70569 Stuttgart, Germany

In histopathology and tumor diagnostics, hematoxylin & eosin (H&E) staining is conventionally used to visualize cells in tissues. Hematoxylin specifically binds to nucleoproteins resulting in blue coloration of the cell nuclei in bright-field microscopy. Although being a gold standard, H&E staining is an invasive technique and one cannot harness quantitative information of, for instance, nucleic acid densities. To circumvent these limitations, a label-free and quantitative imaging technique exploiting the intrinsic biomolecular vibrations of cellular species is desirable. In this work, we demonstrate the quantitative mapping of nucleic acid densities within the nuclei of adipocytes, keratinocytes and endothelial (HDMEC) cells by using confocal Raman microspectroscopy. These are some of the typical cells found in different layers of skin. We have identified the backbone phosphodiester and nucleobases' ring breathing vibrations as unique nucleic acid markers. The proposed method offers the potential for a label-free, rapid and quantitative mapping of nuclei in tissues by means of coherent Raman scattering microscopy and its application in tumor diagnostics.

MO 14.3 Wed 16:30 Poster.IV

IR/UV investigations on aluminum containing peptides — ●TOBIAS MARTIN, PHILIP BIALACH, and MARKUS GERHARDS — TU Kaiserslautern, Physikal. und Theoret. Chemie, 67663 Kaiserslautern

The interplay of peptides with metal ions is of great interest to obtain information on e.g. ion transport. In order to figure out different binding motifs in metal/peptide clusters the attachment of Al⁺ and Al³⁺ cations to the backbone of different protected amino acids and dipeptide models is investigated by means of mass selective IR photodissociation spectroscopy. In case of clusters with very strong bonds between the aluminum cation and an amino acid containing an aromatic chromophore a new variant of combined IR+UV spectroscopy is applied in order to yield the vibrational spectra in the NH stretching region. The comparison with extensive ab initio and DFT calculations leads to suggestions for structural arrangements. The aluminum cations are attached to the carbonyl groups and lead to strong changes of the backbone conformation. The structures are discussed with respect to their stability, spin state and the influence of the aromatic chromophore.

MO 14.4 Wed 16:30 Poster.IV

Probing ultrafast dynamics in biomolecules in natural environment using time-resolved photoelectron spectroscopy —

●MARTIN ECKSTEIN¹, JULIUS ZIELINSKI¹, JOHAN HUMMERT¹, LUCA POLETTO², OLEG KORNILOV¹, and MARC VRAKING¹ — ¹Max-Born-Institut, Berlin — ²Luxor, Padua

We report on the current status of the project, devoted to investigation of ultrafast electron dynamics in molecules and proteins that play a key role in photoactive biological systems. Recently these systems have been under active investigation using all-optical techniques. With the new advances in XUV pulse generation and liquid phase photoelectron spectroscopy we can now study these dynamics by means of Vis-XUV Pump-Probe Photoelectron spectroscopy. We are implementing a time-compensated monochromator to produce ultra short XUV pulses from a high order harmonic source and a liquid water jet technology to bring solvated biomolecules in vacuum for photoelectron spectroscopy study. The setup will allow us to map the electron dynamics of the photoexcited system onto photoelectron spectrum with sub-10fs time resolution and probing valence and inner-valence states in the range of 15 to 50 eV. Advantages of the technique, first results with small solvated chromophores and prospects of detecting quantum coherent effects, that have been recently found in the energy transport in light harvesting complexes, are discussed.

MO 14.5 Wed 16:30 Poster.IV

Energy Transfer and Optical Spectra of the Fenna-Matthews-Olson Complex: Application of NMQSD Master Equation —

●GERHARD RITSCHEL¹, JAN RODEN², WALTER T. STRUNZ³, and ALEXANDER EISFELD⁴ — ¹Max-Planck-Institut für Physik komplexer Systeme, Dresden, Germany — ²University of California, Berkeley, USA — ³Technische Universität Dresden, Germany — ⁴Harvard University, Cambridge, USA

A master equation derived from non-Markovian quantum state diffusion [1] is used to calculate the excitation energy transfer and optical spectra of the photosynthetic Fenna-Matthews-Olson complex at various temperatures [2]. This approach allows us to treat spectral densities that explicitly contain the coupling to internal vibrational modes of the chromophores. Moreover, the method is very efficient making systematic investigations with respect to parameter variations tractable.

Particular attention is paid to the recently discovered eighth chromophore, which is believed to play an important role in receiving excitation from the main light harvesting antenna. When site 8 is excited initially, we see a slow exponential-like decay of the excitation which is in contrast to the oscillations and a relatively fast transfer that usually occurs when initialization at sites 1 or 6 is considered [3]. We show that different sets of electronic transition energies can lead to large differences in the energy transfer dynamics and to different linear spectra.

[1] Roden et al. PRL 103, 058301 (2009)

[2] Ritschel et al. NJP 13, 113034 (2011)

[3] Ritschel et al. JPCL 2, 2912 (2011)

MO 14.6 Wed 16:30 Poster.IV

Spectroscopy of Single Perylene Bisimide Trimers: How Bright States Report About Dark States — ●ABEY ISSAC¹,

RICHARD HILDNER¹, CATHARINA HIPPIUS², FRANK WÜRTHNER², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV and Elite Network of Bavaria (ENB), University of Bayreuth, 95447 Bayreuth, Germany — ²Institut für Organische Chemie and Röntgen Research Center for Complex Material Systems, Universität Würzburg, 97074 Würzburg, Germany

We investigate the fluorescence of single perylene bisimide (PBI) triads linked by two calix[4]arene units, embedded in a polymer matrix. Emission time traces of single triads recorded at room temperature show discrete signal levels which probably reflect the radicalization of individual monomer units. This suggests that the electronic excitations are mainly localized on a monomer unit (weak coupling regime). Emission from such localized states carries information about the neighboring charged (dark) PBI units. In order to extract this information, we recorded along with the fluorescence intensity as a function of time both the fluorescence lifetime and the emission spectrum. Correlations between these observables allow us to characterize the nature of the dark (radical) state.

MO 14.7 Wed 16:30 Poster.IV

Polarization resolved fluorescence excitation spectroscopy of individual chlorosomes from wild type *Chlorobaculum*

tepidum — ●MARC JENDRNY¹, THIJS J. AARTSMA², and JÜRGEN KÖHLER¹ — ¹Chair of experimental physics IV, University of Bayreuth, Germany — ²Department of Biophysics, University of Leiden, Netherlands

We investigate the photophysical processes in chlorosomes which are the main light-harvesting antennae complexes in green photosynthetic bacteria. These complexes feature a rod-like shape of 100 nm - 200 nm length and 20 nm - 50 nm width and consist of bacteriochlorophyll *c*, *d* or *e* depending on the species. The major difference from other light harvesting complexes is that the chromophores are not embedded into a protein-scaffold but self-assemble into aggregates. It is assumed that these antenna complexes vary significantly in size and structure (alignment of chromophores).

We measured polarization-resolved spectra of several individual Chlorosomes of the green sulfur bacterium *Chlorobaculum tepidum* by fluorescence excitation spectroscopy at low temperature (1.5 K) to avoid inhomogeneous broadening. A global fit of the polarisation resolved spectra reveals at least two contributions to the broad absorption at around 750 nm.

MO 14.8 Wed 16:30 Poster.IV

Enantiosensitive Lasermassenspektrometrie: Weiterentwicklung und Spektroskopie — ●KATHARINA TITZE, CHRISTOPH LOGÉ und ULRICH BOESL — Technische Universität München, Department Chemie, Lehrstuhl Physikalische Chemie I, Lichtenbergstraße 4, 85748 Garching

Die enantiosensitive Lasermassenspektrometrie ist eine Methode zum selektiven Nachweis chiraler Moleküle mittels Lasermassenspektrometrie. Sie ermöglicht strukturelle und spektroskopische Untersuchungen wie auch die Bestimmung von Enantiomerenüberschüssen in Stoffgemischen. Die fortlaufende Weiterentwicklung der Methode hat zu einer stetigen Verbesserung der Nachweisgrenzen geführt. Dies konnte an einer erweiterten Zahl an Testsubstanzen gezeigt werden, dabei ist eine Validierung durch den Vergleich von Messungen mittels klassischer Zirkulardichroismus-Spektroskopie möglich. Die neuesten Untersuchungen beschäftigen sich mit dem Einsatz aktiver optischer Elemente zur Erzeugung zirkular polarisierten Lichtes. Bisher eingesetzte Verzögererplatten wurden durch Pockelszellen ersetzt, der Einsatz von photoelastischen Modulatoren ist geplant. Hierdurch lassen sich systematische Abweichungen der Messungen verhindern, welche wiederum die Reproduzierbarkeit und die Nachweisgrenzen beeinflussen. Neben der technologischen Weiterentwicklung wurde das Augenmerk auf spektroskopische Untersuchungen gerichtet. Erwähnenswert sind hier der Zweiphotonen-Zirkulardichroismus sowie Untersuchungen an Überschallstrahlensystemen. Beide Methoden versprechen interessante Ergebnisse über chirale Molekülstrukturen und deren Dynamik.

MO 14.9 Wed 16:30 Poster.IV

Improved potential energy curve of the $X^1\Sigma_g^+$ state of Mg_2 — ●HORST KNÖCKEL, STEFFEN RÜHMANN, and EBERHARD TIEMANN — QUEST und Inst.f. Quantenoptik, Leibniz Universität Hannover

Alkaline earth atoms are candidates for the development of optical clocks because of their narrow optical transitions promising much higher frequency stability and accuracy than for the present Cs-based microwave clocks. For ultimate accuracy the cold collision properties of the atoms must be known. Thus precise knowledge of the molecular potential energy curves (PEC) is important. For Ca_2 and Sr_2 ground and excited states have been characterized precisely while the information for Mg_2 is less complete. For the investigation Mg_2 vapor was produced in a heat pipe and absorption spectroscopy with a UV Fourier transform spectrometer yielded a dense spectrum, which was analyzed with a dedicated computer program to account for the severe overlap of lines due to the various isotopologues and the high temperature population distribution of molecular levels. These measurements were extended with additional recordings of laser induced fluorescence from UV lines of an Ar^+ laser and from a frequency doubled Ti:Sa laser, whose frequencies were selected to characterize levels of the ground state as close as possible to the dissociation limit. The accuracy of the line frequencies is better by about a factor of four compared to previous work. The transition frequencies were modeled by potential energy curves for both upper and lower states. For the ground state various PEC models and for the upper state the present status of evaluation will be presented.

MO 14.10 Wed 16:30 Poster.IV

Angular distribution of photoelectrons of H_2 and its dependence on the internuclear distance — ●UTE LENZ¹, TILL

JAHNKE¹, MARKUS SCHÖFFLER^{1,2}, THORSTEN WEBER², JASMIN TITZE¹, NADINE NEUMANN¹, HENDRIK SANN¹, CHRISTIAN STUCK¹, MATHW JONES⁴, SANKAR DE³, ALI BELKACEM², A L LANDERS⁴, C L COCKE³, and REINHARD DÖRNER¹ — ¹IKF, University of Frankfurt, D-60438 Frankfurt, Germany — ²LBNL, Berkeley CA 94720 — ³Dept. of Physics, KSU, Cardwell Hall, Manhattan KS 66506 — ⁴Dept. of Physics, Auburn AL-36849

In the ground state, the internuclear distance of diatomic molecules oscillates around its mean value. The dependence of the photoelectron angular distribution on this distance was analyzed using data measured with COLTRIMS[1] at the Advanced Light Source. Circularly polarized photons were used to doubly ionize hydrogen molecules. After emission of both electrons, the molecule fragments into two positively charged protons. The internuclear distance during the absorption of the photon is antiproportional to the kinetic energy of the remaining H^+ ions, namely the KER[3]. To look a bit closer at the dependence of the photoelectron distribution on the KER, the experiment was also performed with linearly polarized photons. The photoelectrons are then only able to leave the molecule parallel but never perpendicular to the polarization vector of the electric field [4]. References: [1] R. Dörner et al., 2000, Phys. Rep. 330 95-192 [2] K. Kreidi et al., 2008, PRL, 100:133005 [3] T. Weber et al., 2004, Nature, 431:437*440 [4] M. S. Schöffler et al., 2008, PRA 013414

MO 14.11 Wed 16:30 Poster.IV

Absorption spectroscopy and deperturbation with Sr_2 — ●ALEXANDER STEIN, HORST KNÖCKEL, and EBERHARD TIEMANN — Institut für Quantenoptik, Leibniz Universität Hannover, Welfengarten 1, 30167 Hannover

Ultracold Sr_2 molecules might offer good opportunities for new and exciting experiments like the detection of the time variation of the electron-proton mass ratio (T. ZELEVINSKY AND S. KOTOCHIGOVA AND J. YE, *Phys. Rev. Lett.* **100**, 043201 (2008)). For the production of ultracold molecules in deeply bound rovibrational levels of the ground state, a precise knowledge of intermediate levels of suitable excited electronic states is necessary. As shown in our recent publication on this molecule (A. STEIN AND H. KNÖCKEL AND E. TIEMANN, *Eur. Phys. J. D* **64**, 227 (2011)), the excited states of this molecule are strongly perturbed and thus a high amount of data is necessary for a reasonable description of the coupled systems.

We now report on the usage of a highly efficient method for obtaining precise level energies from a broad band absorption spectrum recorded by a Fourier-transform spectrometer. The method is capable to assign lines in such dense spectra applying the precise knowledge of the electronic ground state. Results of a deperturbation analysis on the coupled system $2^1\Sigma_u^+ - 1^1\Pi_u$ will be presented.

MO 14.12 Wed 16:30 Poster.IV

Multiphoton ionization and fragmentation of HCl: A competition of different pathways leading to H^+ , Cl^+ , HCl^+ and Cl^- . — MICHAEL SCHILLER, ASYLKhan RAKHYMZHAN, ALEXEY CHICHININ, SEBASTIAN KAUCZOK, KARL HEINZ GERICKE, and ●CHRISTOF MAUL — Institut für phys. und theo. Chemie, TU Braunschweig, Germany

HCl exhibits a complex fragmentation and ionization behavior upon resonant photoexcitation of its Rydberg electronic states at around 10 eV. REMPI/TOF techniques and 3D Velocity Map Imaging were used to state selectively determine product yields and photoproduct kinetic energy and angular distributions. The total energy range is 15 to 20 eV, depending on a 3 or 4 photon excitation pathway with photons in the UV wavelength range. Special emphasis is laid on the intermediate state $B^1\Sigma^+$ which is reached via 2 photon absorption from the HCl ground state $X^1\Sigma^+$. This intermediate Rydberg state holds a double minimum potential due to the mixing among the $V^1\Sigma^+$ and $E^1\Sigma^+$ states. A further UV-photon initiates the competition between ionization and fragmentation processes. Repulsive Rydberg states are likely to cause the fragmentation and lead to slow H^+ and Cl^+ ions. The competing pathways via an ion pair state or the ionic ground state lead to faster H^+ ions as well as to HCl^+ and Cl^- . An intriguing case is the Cl^- anion resulting from the photodissociation of the neutral HCl precursor. Belonging to the ion-pair state, it has so far not been detected directly, but was assigned by the analysis of various $V^1\Sigma^+ - X^1\Sigma^+$ (v,0) transitions, which will also be regarded.

MO 14.13 Wed 16:30 Poster.IV

The $B^1\Pi$ and $D^1\Pi$ states in LiRb — ALEXANDER STEIN², MILENA IVANOVA¹, ●ASEN PASHOV¹, HORST KNÖCKEL², and EBERHARD

TIEMANN² — ¹Sofia University St. Kliment Ohridski, Faculty of Physics, 5 J. Bourchier Blvd., 1164 Sofia, Bulgaria — ²Institut fuer Quantenoptik, Leibniz Universitaet Hannover, Welfengarten 1, D-30167 Hannover, Germany

The LiRb molecule has been studied at high resolution by Fourier-transform spectroscopy of laser induced fluorescence. In this contribution we present the analysis on the excited states B¹II and D¹II. The experimental data came from the directly laser induced fluorescence (LIF) spectra, but also from the analysis of the collisionally induced rotation relaxation of the LIF lines. We present the current status of the analysis of the energy levels positions along with a theoretical model for their description.

The D¹II state was observed for the first time during this study. Although less numerous compared to the observations of the B state, the collected experimental data allow for determining a potential energy curve. The influence of possible perturbations will be discussed for their origin.

MO 14.14 Wed 16:30 Poster.IV

Experimental study of excited electronic states in LiCa — MILENA IVANOVA¹, ALEXANDER STEIN², ●ASEN PASHOV¹, HORST KNOECKEL², and EBERHARD TIEMANN² — ¹Faculty of Physics, Sofia University St. Kl. Ohridski, 5 James Bourchier Boulevard, 1164 Sofia, Bulgaria — ²Institut fuer Quantenoptik, Leibniz Universitaet Hannover, Welfengarten 1, D-30167 Hannover, Germany

The 4²Σ⁺ → X²Σ⁺ system in LiCa has been studied by Fourier Transform Spectroscopy. Here we present the analysis of the excited 4²Σ⁺ state. Abundant dataset allowed us to construct accurate potential curve and to explain also the effective spin-rotation splitting of the rotational energy levels.

Another band system in LiCa was also studied, namely the 2²Π-X²Σ⁺. This system has been already observed in absorption (L.M. Russonet et al., J. Chem. Phys. 109, 6655 (1998)) but we were not able to detect any fluorescence when exciting at the reported transition frequencies. In this contribution we discuss the possible reasons.

MO 14.15 Wed 16:30 Poster.IV

Relativistic time-dependent density functional theory, a study of the ground and excited states of the zinc dimer — ●OSSAMA KULLIE — CNRS et Universit'e de Strasbourg, Institut de Chimie, Laboratoire de Chimie Quantique, 1 Rue Blaise Pascal, F-67008 STRASBOURG cedex, France

In this poster I present a (time-dependent) density functional study of the 20 low-lying excited states as well the ground states of the zinc dimer Zn₂. I analyze the spectrum of the dimer obtained from all electrons calculations which are performed using time-dependent density functional with a relativistic 4-components-, and spin-free-Hamiltonian. I will show results for different well-known density functional approximations, in comparing with literature and experimental values, the results are very encouraging, especially for the lowest excited states of these dimers. However, the results show that only the long-range corrected functionals such CAMB3LYP gives the correct asymptotic behavior for the higher states, for which the best result is obtained, and a comparable result is obtained from PBE0 functional.

MO 14.16 Wed 16:30 Poster.IV

Temperature jump apparatus for kinetic terahertz absorption spectroscopy — ●TRUNG QUAN LUONG, ERIK BRÜNDERMANN, and MARTINA HAVENITH — Department of Physical Chemistry II, Ruhr-University Bochum, Germany

We set up a temperature jump (T-jump) apparatus to generate fast T-jump in aqueous solutions for real-time kinetic study. High power short laser pulses (40 mJ/pulse, 5 ns bandwidth) are focused on an aqueous sample to initiate a fast increase in temperature and disturb an existing chemical equilibrium. The kinetics is probed by terahertz time-domain spectroscopy (THz-TDS) which is a sensitive method to observe intermolecular water dynamics. Reproducible T-jumps of 5-7°C are monitored directly by measuring the temperature dependent change in THz absorption of water. The sudden increase in temperature leads to a significant and measurable change of investigated proteins (from folding to unfolding state or vice versa) and their hydration shell. The first combination between T-jump and THz-TDS provides opportunities to probe protein folding dynamics through its coupled water dynamics in the hydration shell.

MO 14.17 Wed 16:30 Poster.IV

Toward atomic resolution X-ray imaging of isolated molecules — ●STEPHAN STERN^{1,2}, JOCHEN KÜPPER^{1,2}, HENRY CHAPMAN^{1,2}, and DANIEL ROLLES³ — ¹Center for Free-Electron Laser Science (CFEL), DESY, Hamburg — ²University of Hamburg — ³Max Planck Advanced Study Group at CFEL, Hamburg

X-ray diffractive imaging is an indispensable tool in science, i.e., for examination of the structure of matter and complex molecules. X-ray Free-Electron Lasers allow for ultrafast time-resolved diffractive imaging of, for example, nanocrystals or individual viruses. Here, we present first results on the diffractive imaging of controlled – state-, size-, and isomer-selected and strongly aligned – ensembles of individual gas-phase molecules. We have performed the first corresponding experiments using LCLS at SLAC on diiodobenzonitrile and will present details on the experimental realization, the theoretical background, and a detailed analysis of the obtained experimental data.

This work was carried out within a collaboration, for which J. Küpper, H. Chapman and D. Rolles are spokespersons. The collaboration consists of CFEL (DESY, MPG, University Hamburg), Fritz-Haber-Institute Berlin, MPI Nuclear Physics Heidelberg, MPG Semiconductor Lab, PNSensor GmbH, Aarhus University, FOM AMOLF Amsterdam, Lund University, MPI Medical Research Heidelberg, TU Berlin, Max Born Institute Berlin, and SLAC Menlo Park USA. The experiments were carried out using CAMP (designed and built by the MPG-ASG at CFEL) at the LCLS (operated by Stanford University on behalf of the US DOE.)

MO 14.18 Wed 16:30 Poster.IV

Single-beam-CARS using broadband shaped laser pulses — ●ALEXANDER WIPFLER, JEAN REHBINDER, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

CARS microscopy has proven to be a powerful tool for the imaging of biological and chemical samples. In single-beam-CARS experiments all photons involved in the signal generation stem from one laser pulse which decreases the experimental demands. As the accessible Raman range is limited by the excitation bandwidth, short pulses with broad spectra are desirable. Therefore special care has to be taken in pulse compression. We present a new single-beam-setup using a light source consisting of no more than a commercial sub-10fs-Ti:Sa-oscillator and a pulse shaper that is able to detect the entire relevant vibrational Raman spectrum from the fingerprint up to the CH-stretching region. As one excitation scheme, the control of the Raman excitation is presented in theory and demonstrated experimentally on neat liquid samples. Another approach is the multiplexing of single-beam-CARS by the introduction of a narrowband feature in the excitation spectrum. This is demonstrated in chemical selective imaging of moss cells and in the full determination of the third-order nonlinear susceptibility.

MO 14.19 Wed 16:30 Poster.IV

A sample holder for soft x-ray absorption spectroscopy of liquids in transmission mode — ●SIMON SCHRECK, CHRISTIAN WENIGER, GIANINA GAVRILA, and PHILIPPE WERNET — Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin, Germany

Applying soft x-rays to liquids is challenging due to the incompatibility of the vacuum environment required for soft x-rays and the high vapor pressure of liquids. When recording soft x-ray absorption spectra in transmission mode, which is the most direct and efficient way, the strong attenuation of soft x-rays in matter calls for ultrathin samples.

Here we present a novel sample holder for soft x-ray absorption spectroscopy of liquids in transmission mode based on sample cells with x-ray transparent silicon nitride membranes. The sample holder allows for a reliable preparation of ultrathin liquid films with an adjustable thickness in the nm-μm range. This enables measurements of high quality x-ray absorption spectra of liquids in transmission mode, as will be shown for the example of liquid H₂O, aqueous solutions of 3d-transition metal ions and alcohol-water mixtures. The fine structure of the x-ray absorption spectra is not affected by the sample thickness. No effects of the silicon nitride membranes were observed in the spectra. It is shown how an inhomogeneous thickness of the sample affects the spectra and how this can be avoided.

The measurements were performed at the synchrotron radiation source BESSYII at the Helmholtz-Zentrum Berlin.

MO 14.20 Wed 16:30 Poster.IV

First time-resolved pump-probe experiments at PETRA III using a synchronized highly repetitive multi-frequency

laser system — ●MORITZ SCHLIE^{1,2}, DENNIS GÖRIES², BENJAMIN DICKE², ARMIN AZIMA¹, MAREK WIELAND¹, JENS VIEFHAUS², ALKE MEENTS², and MARKUS DRESCHER¹ — ¹Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany — ²Deutsches Elektronen Synchrotron, Notkestraße 85, 22609 Hamburg

To enable laser / X-ray pump-probe experiments at the new PETRA III synchrotron radiation facility at DESY, a synchronized laser system has been set up. Wavelengths ranging from 210 nm to 2600 nm are delivered at a high repetition rate of 130 kHz, thus allowing highly efficient experiments with flexible excitation schemes. The system is based on a commercial diode-pumped Yb:KGW laser with 6 W output power followed by an Optical Parametric Amplifier and Harmonic Generation modules. The laser is synchronized with one electron bunch in the ring. To this end, phase locked loops (PLL) lock the laser's oscillator frequency (83 MHz) and its 6th harmonic to the PETRA III master oscillator (500 MHz) and its 6th subharmonic allowing furthermore the setting of fine and coarse delays. The synchronization and delay-scheme are presented together with first time resolved experiments performed at beamline P11.

MO 14.21 Wed 16:30 Poster.IV

Concentrated nanoparticle beams for optical and X-Ray spectroscopy — ●MARKUS ERITT¹, DENIS DUFT², and THOMAS LEISNER^{1,2} — ¹Institute for Environmental Physics, Ruprecht-Karls-University Heidelberg, Germany — ²Institute for Meteorology and Climate Research, Karlsruhe Institute of Technology (KIT), Germany

Our setup provides free nanoparticles in a size range from 3 to 10 nm in diameter for spectroscopic investigations. Nanoparticles dispersed in a carrier gas and sampled from ambient air or a reservoir at pressures from 10 to 1000 mbar are transferred to UHV-conditions using an aerodynamic lens inlet. By concentrating the charged particles in an electrodynamic cage particle densities of up to $10E8$ 1/cm³ are reached. Cavity enhanced absorption spectroscopy is used for the determination of optical constants and time-of-flight spectroscopy in combination with an ultra-short-pulse laser system for mass determination. High density particle bunches extracted from the cage allow the application of core level photoelectron spectroscopy at synchrotron sources. In this contribution we will describe the setup and its function. The main perspective of this apparatus are observations on mesospheric processes (e.g. ice growth on nanometric seeds) under realistic atmospheric conditions.

MO 14.22 Wed 16:30 Poster.IV

The electric deflector – a state selector for complex molecular systems — YUAN-PIN CHANG¹, SEBASTIAN TRIPPEL¹, ●ZEINAB ESKANDARIAN¹, TERENCE G. MULLINS¹, STEPHAN STERN¹, LOTTE HOLMEGARD¹, KAROL DŁUGOLECKI¹, and JOCHEN KÜPPER^{1,2} — ¹Center for Free-Electron Laser Science, DESY, Hamburg — ²University of Hamburg

Size and state selection of molecules by means of electric deflection is an important, recently rejuvenated topic in molecular beam studies. The force exerted on a neutral polar molecule by an inhomogeneous electric field can be exploited to spatially separate quantum states due to their individual effective dipole moments. This state-selection has been used to experimentally create extremely polar samples for alignment and orientation control, as well as for the separation of structural isomers of complex molecules. In this contribution we will discuss the optimal shape of the device regarding its selectivity.

We will discuss the already obtained as well as the potential selectivity on a theoretical and experimental investigation of the separation of a single species from a cluster coexpansion of water and indole, resulting in a modestly cold beam (~ 5 K) of water, indole, indole(H₂O) and indole(H₂O)_n ($n \geq 2$). Specifically, we have created a pure sample of the indole-water 1:1 complex using the Chamberlain deflector design. We evaluate (computationally) the improvements in the selectivity – for this and other species from the expansion – that are possible using improved mechanical designs.

MO 14.23 Wed 16:30 Poster.IV

Time resolved XAS of Gaq3 at new PetraIII beamline P11 — ●BENJAMIN DICKE¹, DENNIS GOERIES¹, MORITZ SCHLIE², ALKE MEENTS¹, and EDGAR WECKERT¹ — ¹Deutsches Elektronen Synchrotron (Desy) - HASYLAB, Notkestrasse 85, D-22607 Hamburg, Germany — ²Institute for Experimental Physics, University of Hamburg, Luruper Chaussee 149, D-22761 Hamburg, Germany

Metalorganic compounds such as tris(8-hydroxyquinoline) gallium (Gaq3) are promising materials for the emission layer of Organic light emitting diodes (OLEDs) due to their specific electro- and photoluminescent properties. Many studies have been done to understand the mechanisms of electroluminescence in order to develop new emitter materials and thus optimized OLEDs with higher efficiency. Nevertheless the excited state structure remains unknown. To determine the excited state structure of metalorganic compounds a setup for time resolved X-ray absorption spectroscopy (XAS) has been developed. The compound in solution-phase is passed through a nozzle of 30 μ m diameter to form a free-standing micro-jet. A pulsed laser which is synchronized to the synchrotron is focused on the micro-jet and excites the flowing molecules. The X-ray is directed on the jet so that X-ray focus and laser focus are overlapping. In this way the excited states of the molecules are probed. We show first results towards time resolved XAS of Gaq3.

MO 14.24 Wed 16:30 Poster.IV

Soft x-ray emission spectroscopy on liquid jets - probing valence structure of solvents and solutes — ●KRISTJAN KUNNUS¹, MARTIN BEYE¹, ALEXANDER FÖHLISCH¹, SEBASTIAN GRÜBEL², FRANZ HENNIES³, CHRISTIAN KALUS¹, KERSTIN KALUS¹, BRIAN KENNEDY³, WILSON QUEVEDO¹, IVAN RAJKOVIC², SIMON SCHRECK¹, EDLIRA SULJOTI¹, SIMONE TECHERT², CHRISTIAN WENIGER¹, and PHILIPPE WERNET¹ — ¹Helmholtz-Zentrum Berlin, Berlin, Germany — ²Max Planck Institute for Biophysical Chemistry, Göttingen, Germany — ³MAX-lab, Lund, Sweden

We have developed an experimental set up which combines an in vacuum liquid jet with a soft x-ray emission spectrometer to enable resonant inelastic soft x-ray scattering (RIXS) measurements from liquids. RIXS is a powerful technique which enables to probe occupied and unoccupied electronic states with elemental and chemical selectivity. Advantages of using a liquid jet are continuous replenishment of the sample and absence of membranes to separate the liquid from the vacuum. These properties make the setup suitable for complementary usage at synchrotrons and x-ray free electron laser facilities. As example, RIXS L-edge spectra of K₃[Fe(CN)₆] and CrCl₃ aqueous solutions together with K-edge spectra of bulk water and alcohols are presented. These measurements were done at the BESSYII synchrotron radiation facility in Berlin, Germany.

MO 14.25 Wed 16:30 Poster.IV

Raman Experimental Evidence for CTAB-Chain Bending within Clay – Generalized Concept of Conformation Reorganization in Long CH₂ Chains Embedded within Modified Clay — ●PATRICE DONFACK¹, ELENA A. SAGITOVA^{1,2}, KIRILL A. PROKHOROV², GOULNARA YU. NIKOLAIEVA², VIKTOR A. GERASIN³, NADEZHDA D. MEREKALOVA³, EVGENY M. ANTIPOV³, PAVEL P. PASHININ², and ARNULF MATERNY¹ — ¹Research Center of Functional Materials and Nanomolecular Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany — ²A.M. Prokhorov General Physics Institute of RAS, Moscow, Russia — ³A.V. Topchiev Institute of Petrochemical Synthesis of RAS, Moscow, Russia

We have studied the CH₂-chain bending in connection with the conformation reorganization and switching within long CH₂-chain molecules confined in modified clay interlayers. Besides different other observations, specifically Raman spectra give strong evidence for the bending within the galleries of clay modified by cetyltrimethylammonium bromide (CTAB)-chains; CTAB consists of single CH₂-chains. As also suggested by computational modeling, the CH₂-chain bending results in a splitting of the symmetric C-C stretching Raman mode into two subbands, indicating the coexistence of two nonequivalent (in length and terminal group) CH₂-chain trans-segments within the alkylammonium ion embedded in the clay interlayer space. The monitoring of modifier content-dependent interlayer conformational states is demonstrated. This is important for fabricating modified clays-based nanocomposites with desired properties in a tunable way.

MO 14.26 Wed 16:30 Poster.IV

Surface-Enhanced Raman Spectroscopy (SERS) for BTEX Detection — ●RASHA HASSANEIN, BERND VON DER KAMMER, and ARNULF MATERNY — Research Center for Functional Materials and Nanomolecular Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany

Raman spectroscopy gives access to the vibration fingerprint of molecules even for complex samples in liquid, solid, and gas phase. The inherent low signal intensity of Raman scattering, which limits

the detectable concentration, can be drastically enhanced by a surface enhancement (SE) effect. In SE Raman spectroscopy (SERS), field enhancement is occurring for molecules adsorbed to rough (nanostructured) surfaces of coinage metals such as Ag, Au, or Cu. In this contribution, we report the application of SERS for the detection of traces of contaminations of water. A particular problem are benzene, toluene, ethylbenzene, and xylene (BTEX), which are volatile organic compounds found *e.g.* in petrol, contaminating ground and surface water. A technique, which is sensitive, rapid, and selective is required in order to detect the traces of BTEX. We have applied different SERS techniques and achieved a detection limit for BTEX of 500 ppb in combination with a visible laser excitation source. In our contribution we discuss the different approaches and present the SERS results.

MO 14.27 Wed 16:30 Poster.IV

Raman Spectroscopy Techniques for the Detection of Explosives — ●RASHA HASSANEIN, BERND VON DER KAMMER, and ARNULF MATERNY — Research Center for Functional Materials and Nanomolecular Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany

The detection of explosives and compounds used for the synthesis of explosive substances attracts considerable attention. In our work, we have applied different Raman spectroscopy techniques in order to identify explosive-related molecules with high sensitivity and fingerprint selectivity. Here, we present results of Raman spectroscopy applied to perchlorate anions in water. Traces of this highly explosive substance have been detected in ground water, soil and drinking water as a result of its use as main component in missile and rocket fuel. Consumption of perchlorate in drinking water interferes and disturbs the function of the thyroid gland, which then leads to secondary diseases. Techniques applied to increase the sensitivity were surface-enhanced Raman spectroscopy (SERS), which makes use of local field enhancement close to metal nanoparticles, as well as accumulation techniques, increasing the concentration within the interaction range of the excitation laser. Best results were obtained using resin beads - insoluble polymer particles - which attract the anions via an ion exchange process. With adapted resin beads we were able to detect perchlorate traces down to approx. 1 ppb concentration.

MO 14.28 Wed 16:30 Poster.IV

Wigner Function Reconstruction in the Talbot Regime — ●CAROLA SZEWC¹, SUN KYUNG LEE², MYUNGSHIK KIM², and HENDRIK ULBRICHT¹ — ¹University of Southampton, Highfield, SO17 1BJ Southampton, UK — ²QOLS, Blackett Laboratory, Imperial College London, UK

We theoretically investigate the possibility of Wigner function reconstruction of the motional quantum state of heavy molecules in the near-field Talbot-Lau regime. In general, the reconstruction of the Wigner distribution function is important to test quantum states on their properties such as entanglement, superposition and coherence. The wave nature of molecules has been demonstrated by interferometry. We aim to make the next step to extract sufficient information about the motional quantum state to evidently show a superposition signature of the associated Wigner function. We therefore report on the reconstruction of this quasi-probability function under considera-

tion of experimental conditions, such as a finite number of slits, the limited collimation of the particle beam and the particle-grating van der Waals interaction. We still find sufficient information to reconstruct a Wigner function with a meaningful structure and negative values.

MO 14.29 Wed 16:30 Poster.IV

Experimental imaging of non-adiabatic coupling in a triatomic molecule — ●PEER CORNELIS FECHNER, KAI MOZER, and HANSPETER HELM — Physikalisches Institut, Albert-Ludwigs-Universität Freiburg

Due to its simple structure, the neutral triatomic hydrogen molecules H₃ and D₃ are model-systems for the intramolecular dynamics in polyatomic molecules. We find these dynamic features encoded in correlations of the atom-momentum-vectors emerging from 3-body-decay of state selected molecules, H₃ → H(1s) + H(1s) + H(1s). Fragmentation is induced by non-adiabatic couplings. By collecting the temporal and spatial information of triple-coincidence fragment atoms from isolated molecules, we deduce the center-of-mass momentum-vector correlation (MVC) which we represent in Dalitz-plots. Here we undertake a thorough comparison of experimental MVCs of different vibrational 2sA₁'-states of H₃ and D₃ with predictions from a theoretical model [1,2]. The agreement of modeled and measured MVCs impressively shows that the vector correlations are direct images of the product of the vibrational wavefunction and the spatial dependence of the non-adiabatic coupling operator responsible for the dissociation. Our comparison also indicates that propagation of the hydrogen atoms on the dissociative ground potential-surface plays only a minor role in shaping correlation features. Research supported by DFG HE 2525/9.

[1] U. Galster, Phys. Rev. A 81, 032517 (2010)

[2] H. Höffler *et al.*, Phys. Rev. A 83, 042519 (2011)

MO 14.30 Wed 16:30 Poster.IV

Stark effect enhanced dissociation of high Rydberg states in the D₃ molecule — ●KAI MOZER, PEER CORNELIS FECHNER, and HANSPETER HELM — Physikalisches Institut, Albert-Ludwigs-Universität Freiburg

Various terms of non-adiabatic coupling in molecules show a pronounced isotope dependence. This dependence arises primarily from reduced mass effects and to a lesser extent from effects of nuclear spin. In order to examine isotope effects we have undertaken a comparative study of long-lived D₃ and H₃ molecules in high Rydberg states close to the ionization threshold. This energy region has been studied with great scrutiny in dissociative recombination (DR) experiments [2] and for H₃ in a previous study [1]. In our experiment the long-lived Rydberg states ($\tau > 500$ ns) are induced to dissociate by a short electric field pulse experienced by the molecule when it transverse a miniature spatial region of high electric field (up to 20 kV/cm). We monitor in triple coincidence the three-body decay and compare the results of H₃ and D₃. We also compare our findings with observations by Strasser *et al.*, who examined the DR of cold D₃⁺-ions with slow electrons at the TSR [2]. Research supported by DFG HE 2525/9

[1] P. Fechner and H. Helm, Phys. Rev. A 82, 052523 (2010)

[2] D. Strasser *et al.*, Phys. Rev. A 66, 032719 (2002)

MO 15: SYRA: Ultracold Rydberg Atoms and Molecules 3

Time: Thursday 10:30–13:00

Location: V7.03

MO 15.1 Thu 10:30 V7.03

Interaction enhanced imaging of individual Rydberg atoms in dense gases — ●MARTIN ROBERT-DE-SAINT-VINCENT, GEORG GÜNTER, CHRISTOPH S. HOFMANN, HANNA SCHEMPP, HENNING LABUHN, SHANNON WHITLOCK, and MATTHIAS WEIDEMÜLLER — Physikalisches Institut, Universität Heidelberg, Philosophenweg 12, 69120 Heidelberg

Neutral atoms in Rydberg states are highly-polarisable particles, which can experience quantum effects and interactions over macroscopic distances. Many-body systems of Rydberg atoms offer a unique opportunity to create and investigate strong correlations in ultra-cold atomic gases [1]. Until recently, Rydberg ensembles have mostly been studied via field-ionization and subsequent ion detection, typically providing ensemble properties. Here, we present an all-optical method

to image individual Rydberg atoms embedded within dense gases of ground state atoms [2]. The scheme exploits interaction-induced shifts on highly polarizable excited states of probe atoms, which can be spatially resolved via an electromagnetically induced transparency resonance. Using a realistic model, we show that individual Rydberg atoms can be imaged with enhanced sensitivity and high resolution despite photon shot noise and atomic density fluctuations. This scheme could be extended to other impurities such as ions, and is ideally suited to studies of spatially-correlated many-body systems.

[1] Pohl *et al.*, PRL 104, 043002 (2010)

[2] G. Günter *et al.*, arXiv:1106.5443v1 (2011), to be published in PRL

MO 15.2 Thu 10:45 V7.03

Rydberg Atom Spectroscopy in Electric Fields — ●ATREJU

TAUSCHINSKY, RICHARD NEWELL, VANESSA LEUNG, BEN VAN LINDEN VAN DEN HEUVELL, and ROBERT SPREEUW — Institute of Physics, University of Amsterdam, Amsterdam, Netherlands

We study rubidium Rydberg states in static and oscillating electric fields using Electromagnetically Induced Transparency (EIT) in the $5s-5p-n\ell$ system for $n \geq 28$ and $\ell = 0 \dots 2$. We present high-precision Doppler free measurements of DC Stark shifts in a room temperature vapour cell which are in excellent agreement with theoretical calculations. These measurements clearly show that the assumption of quadratically shifting energy levels where the shift is determined by the polarizability of the state is valid only for very small fields, less than 5% of the Inglis-Teller Limit.

We furthermore investigate the behaviour of Rydberg states in superposed AC and DC electric fields and observe populated sidebands of very high order. We present a model, based on generalized Bessel functions for the sideband population induced by oscillating fields in arbitrarily stark-shifting levels and compare the results of this model to our measurements.

Atreju Tauschinsky *et al.* Spatially resolved excitation of Rydberg atoms and surface effects on an atom chip. *Phys. Rev. A* **81**, 063411 (2010)

C. S. E. van Ditzhuizen *et al.* Observation of Stückelberg oscillations in dipole-dipole interactions. *Phys. Rev. A* **80**, 063407 (2009)

MO 15.3 Thu 11:00 V7.03

Coherent spectroscopy involving Rydberg states in electrically contacted microcells — ●RENATE DASCHNER, RALF RITTER, DANIEL BARREDO, HARALD KÜBLER, ROBERT LÖW, and TILMAN PFAU — Universität Stuttgart

Micron sized glass cells filled with atomic vapor are promising candidates for quantum devices based on the Rydberg blockade. Due to the strong interaction between two Rydberg atoms, only one Rydberg excitation is possible within a certain volume characterized by the blockade radius (typically few microns). This effect also provides a nonlinearity that is an essential tool for proposals to entangle mesoscopic ensembles and to realize single photon sources. Measurements show, that coherent Rydberg excitation in thermal vapor and micron-sized cells is possible [1].

The large DC Stark shift of Rydberg atoms provides a possibility to induce transmission or absorption in the medium. To address individual cells one needs electrical contact of the cells. This can be done by coating the inside of glass cells for example with a metal. We show first measurements in coated electrically contacted cells where we can shift the signal by more than one linewidth with a DC electric field.

[1] Kübler, H., Shaffer, J. P., Baluksian, T., Löw, R. & Pfau, T. Coherent excitation of Rydberg atoms in micrometre-sized atomic vapour cells, *Nature Photon.* **4**, 112-116 (2010)

MO 15.4 Thu 11:15 V7.03

Measurement of the Rydberg ionization current in thermal vapor cells — ●DANIEL BARREDO, RENATE DASCHNER, HARALD KÜBLER, RALF RITTER, ROBERT LÖW, and TILMAN PFAU — 5. Physikalisches Institut, Universität Stuttgart, Germany

Rydberg atoms confined in atomic vapor cells are promising candidates for the realization of single photon sources and quantum optical devices [1]. To date, most information about the behavior of the Rydberg ensembles in thermal vapors has been extracted by absorptive measurements, e.g. EIT. However, to access directly quantities, like the population of the excited states, new methods are needed. In this task, the detection of the Rydberg ionization current provides a complementary and direct insight in the atomic processes.

We show measurements of the Rydberg-ion current in thermal vapor cells equipped with field plates.

[1] Kübler, H., Shaffer, J.P., Baluksian, T., Löw, R. and Pfau, T. Coherent excitation of Rydberg atoms in micrometre-sized atomic vapour cells, *Nature Photon.* **4**, 112-116 (2010).

MO 15.5 Thu 11:30 V7.03

Scaling laws and correlations in finite Rydberg gases — ●MARTIN GÄRTTNER^{1,2}, THOMAS GASENZER², and JÖRG EVERS¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, D-69117 Heidelberg — ²Institut für Theoretische Physik, Ruprecht-Karls-Universität Heidelberg, Philosophenweg 16, D-69120 Heidelberg

We study the coherent dynamics of a finite laser-driven cloud of ultracold Rydberg atoms by calculating the time evolution from the full many body Hamiltonian. Using the frozen gas approximation and

treating the atoms as effective two level systems, we are mainly interested in the spatially resolved properties of the gas in its thermalized state. Even for resonant coupling to the Rydberg state, the pair correlation function shows a pronounced structure. It turns out that a simple estimation of the blockade radius predicts the position of the first maximum of the $g^{(2)}$ -function quite well. However, we show that algebraic scaling laws as predicted in [1] are modified by finite size effects which serves as a test of the validity of the super atom picture. At positive detuning crystalline structures are observed even without using chirped laser pulses [2], which can be explained by resonant excitation processes and finite size effects.

[1] H. Weimer *et al.*, *Phys. Rev. Lett.* **101**, 250601 (2008)

[2] T. Pohl *et al.*, *Phys. Rev. Lett.* **104**, 043002 (2010)

MO 15.6 Thu 11:45 V7.03

Coherence on Förster resonances between Rydberg atoms — ●ALEXANDER KRÜPP, JOHANNES NIPPER, JONATHAN BALEWSKI, ROBERT LÖW, and TILMAN PFAU — 5. Physikalisches Institut, Universität Stuttgart

Förster resonances are non-radiative dipole-dipole interactions between oscillating dipoles. Especially in biochemistry these resonances play a crucial role and describe the energy transfer process between two chromophores, parts of molecules which are responsible for their colors. In our work these resonances occur between a pair of Rydberg atoms, creating strong interactions between the atoms.

We report on studies of Förster resonances between Rydberg atoms in an ultra-cold atomic cloud of ⁸⁷Rb. By applying a small electric field we tune dipole coupled pair states into resonance, giving rise to Förster resonances. Via a Ramsey-type atom interferometer we can resolve several resonances at distinct electric field strengths. We study the coherence of the system at and close to the resonances and we observe a change in phase and visibility of the Ramsey fringes on resonance. The individual resonances are expected to exhibit different angular dependencies, opening the possibility to tune not only the interaction strength but also the angular dependence of the pair state potentials by an external electric field. In summary, we now have a tool to coherently tune interactions between Rydberg atoms. In further studies Rydberg atoms could be used as a model system to simulate energy transfer processes in bio-molecules.

MO 15.7 Thu 12:00 V7.03

Collective and quasiparticle excitations in 2D dipolar gases — ●ALEXEY FILINOV und MICHAEL BONITZ — Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität, Leibnizstr. 15, D-24098 Kiel, Germany

The Berezinskii-Kosterlitz-Thouless transition in dipolar atomic, molecular and indirect exciton systems has been recently studied by path integral Monte Carlo simulations [1,2]. Here, we complement these analyses by the spectral densities of the longitudinal collective and single particle (SP) excitations by computing the dynamic structure factor, $S(q, \omega)$, and the SP spectral function, $A(q, \omega)$, across the superfluid to normal fluid transition. The SP spectrum has been worked out by evaluation of the one-particle Matsubara Green's function together with a stochastic optimization method for the reconstruction of $A(q, \omega)$ from imaginary times. We discuss the coupling of both spectra in the *superfluid phase*. We observe sharp resonances due to the quasi-condensate. The excitations in the normal phase are shifted to higher energies and significantly damped beyond the acoustic branch. Our results generalize previous zero-temperature analyses based on variational many-body wavefunctions [2,3]. The underlying physics of excitations and the role of the condensate is not easily extracted from such calculations. Moreover, at finite temperatures the use of the variational approach becomes problematic as the excitation damping becomes significant.

[1] A. Filinov *et al.*, *PRL* **105**, 070401(2010); [2] J. Böning *et al.*, *PRB* **84**, 075130(2011); [3] F. Mazzanti *et al.*, *PRL* **102**, 110405(2009); [4] D. Hufnagl *et al.*, *PRL* **107**, 065303(2011)

MO 15.8 Thu 12:15 V7.03

Crystallization of Rydberg excitations in continuously driven atomic ensembles — ●DAVID PETROSYAN^{1,2} and MICHAEL FLEISCHHAUER¹ — ¹Fachbereich Physik, Technische Universität Kaiserslautern, D-67663 Kaiserslautern — ²Institute of Electronic Structure and Laser, FORTH, GR-71110 Heraklion, Crete, Greece

We study resonant optical excitations of dense atomic ensembles to the strongly interacting Rydberg states. We show that in the steady state of strong continuous driving the correlations of Rydberg excitation probabilities exhibit damped spatial oscillations reminiscent of

the density waves of a finite temperature Luttinger-liquid with Luttinger parameter $K \ll 1/2$. For very strong driving, the period of the spatial oscillations saturates to a value corresponding to one collective Rydberg excitation (superatom) per blockade distance. After sudden switching off of the coupling lasers, the Rydberg quasi-crystal can survive for tens or hundreds of microseconds, it can be detected in situ by spatially-resolved Rydberg state ionization or adiabatically converted into a train of single-photon pulses.

MO 15.9 Thu 12:30 V7.03

Nonlocal Nonlinear Optics in cold Rydberg Gases — ●SEVILAY SEVINÇLI^{1,2}, NILS HENKEL¹, CENAP ATES¹, and THOMAS POHL¹ — ¹Max Planck Institute for the Physics of Complex Systems, 01187 Dresden, Germany — ²Department of Physics and Astronomy, Aarhus University, 8000 Aarhus C, Denmark

Electromagnetically induced transparency (EIT) provides remarkable possibilities for nonlinear optics by enabling ultraslow group velocities and storage of light. The combination of EIT and interacting Rydberg gases has recently attracted considerable theoretical and experimental interest, as it holds promise for realizing extremely large nonlinearities by exploiting the exaggerated interactions between Rydberg atoms.

We present an analytical theory of the nonlinear response of cold Rydberg gases. This yields simple expressions for the third order susceptibilities which are in excellent agreement with recent measurements.

It is further found that the nonlinear susceptibility is not only drastically enhanced but also highly nonlocal in nature, corresponding to long-range photon-photon interactions. Considering the propagation of light in such a Rydberg-EIT medium, this gives rise to a wealth of nonlinear wave phenomena, including soliton formation or modulation instabilities of strongly interacting light fields.

MO 15.10 Thu 12:45 V7.03

Collective interactions in Rydberg-dressed Bose-Einstein condensates — ●NILS HENKEL and THOMAS POHL — Max Planck Institute for the Physics of Complex Systems, Dresden

We investigate a Bose-Einstein condensate where atoms are dressed to high Rydberg states with strong van der Waals interactions. Solving exactly the internal many-body state dynamics, we show that this leads to effective ground state interactions with genuine many-body character. In the limit of large laser detunings, two-body interactions dominate [1,2] while many-body interactions become relevant in the strong-driving limit, i.e. in the limit of large laser intensities or weak detunings. We study the effects of these higher order interactions and show that nonlocal phenomena found for binary interactions are still also observable in the presence of strong collective, i.e. genuine many-body, interactions.

[1] N. Henkel, R. Nath and T. Pohl, *Phys. Rev. Lett.* **104** 195302

[2] F. Maucher et al., *Phys. Rev. Lett.* **106** 170401

MO 16: Collisions and Spectroscopy in He-Droplets

Time: Thursday 10:30–12:30

Location: V38.02

MO 16.1 Thu 10:30 V38.02

Energy transfer in the gas phase collision reaction of $\text{Cl}^- + \text{CH}_3\text{I}$ — ●MARKUS KOWALEWSKI and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwigs-Maximilians Universität München

The bimolecular substitution reaction of chloride and methyl iodine belongs to a fundamental class of chemical reactions. We are motivated by the experimental results of Mikosch et al. [1], which has some open questions. The collision reaction is simulated by solving the time dependent Schrödinger equation on ab initio potential energy surfaces. With the chosen reactive coordinates it is possible to reproduce the basic features of the immediate collision reaction. The energy transfer in the system is investigated and compared to the experimental results. From the new insight into the process, an intuitive concept of a dynamical barrier can be derived. Moreover the role of the spectator mode can be clarified.

[1] J. Mikosch, S. Trippel, C. Eichhorn, R. Otto, U. Lourderaj, J. X. Zhang, W. L. Hase, M. Weidemüller, R. Wester, *Science* **319**, 183 (2008).

MO 16.2 Thu 10:45 V38.02

Rotational Angular Momentum Polarisation of HF in $\text{H} + \text{FCI}(\nu=0-5, j=0-9) \rightarrow \text{HF} + \text{Cl}$ at 0.5-20 kcal/mol — ●VICTOR WEI-KEH WU — Group 1101, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 116023 Dalian, PRChina — Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, 80782 Kaohsiung, Taiwan — Victor Basic Research Laboratory e. V. Gadderbaumer-Str. 22, D-33602 Bielefeld, Germany

Using QCT-PDDCS method, product alignment and orientation on PES of $1^2\text{A}'$ have been studied. HF alignment is found to be, (a) weaker at all collision energies, (b) vibrationally enhanced by the reactant FCl, but for case (c), rather insensitive to initially rotational excitation. The rot. vector of HF orientation pointing to either negative or positive direction of the y-axis in the c.m. frame, e.g. origin of the coordinate system, is enhanced by collision energies, while it becomes weaker at higher vib. ($\nu = 0-5$) or rot. ($j = 0, 3, 6, 9$) excitation levels. Effects of collision energies and of rot. excitation with 15 kcal/mol on the calculated PDDCSs are also shown and discussed. $p(\varphi_r)$ in the range of $0 \leq \varphi_r \leq 360^\circ$, and $p(\vartheta_r, \varphi_r)$ of $0 \leq \vartheta_r \leq 180^\circ$ and $0 \leq \varphi_r \leq 360^\circ$ at 0.5-20 kcal/mol have been presented. Results of PDDCSs of the HF alignment and orientation at these collision energies are not very strongly distinguishable. QCT-PDDCS code from K-L Han, Group 1101 of DICP, and financial aids by VBR in Bielefeld, Germany are acknowledged. Ref. 1. V.W.-K.Wu, M.-Y.Chung, and F.Kure(Ko), *JMS*. 983 (2010) 1; 2. V.W.-K.Wu, *PCCP*. 13 (2011)

9407.

MO 16.3 Thu 11:00 V38.02

Transfer ionization in swift D^+ on H_2 collisions - dependence of the electron emission on the internuclear distance — ●MARKUS WAITZ, HONG-KEUN KIM, JASMIN TITZE, MARKUS S. SCHÖFFLER, TILL JAHNKE, ACHIM CZASCH, LOTHAR PH. H. SCHMIDT, HORST SCHMIDT-BÖCKING, and REINHARD DÖRNER — Institut für Kernphysik, Goethe-Universität Frankfurt, 60438 Frankfurt, Germany

Transfer ionization in swift (several a.u. velocity) ion helium collisions leads to a rich structure in the momentum distribution of the emitted electron. One part of the electrons is emitted in the forward direction, similar to single ionization. This might be associated with a two step process, where two independent interactions of the projectile with either electron leads to capture of one and ionization of the second one. There is however also a strong distinct peak of backward emitted electrons. The underlying mechanism is single capture accompanied by a shake off of the second electron. Here we report on the first experimental observation of transfer ionization on molecular hydrogen. The momentum distribution of the measured electron shows a clear subdivision into forward and backward emission. In addition, we find a surprising dependence of electron emission on the internuclear distance. The forward part of the electron momentum distribution gives higher values for perpendicular orientation of the molecule with respect to the incident beam direction. The SO part does not show this dependence. As a result, the ratio between forward and backward emission changes with internuclear distance.

MO 16.4 Thu 11:15 V38.02

Collision cross sections of state selected $\text{OH} + \text{NO}$ — ●MORITZ KIRSTE, XINGAN WANG, HANS CHRISTIAN SCHEWE, GERARD MEIJER, and SEBASTIAAN VAN DE MEERAKKER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Deutschland

The crossed molecular beam technique is a mature and important experimental method to understand molecular interactions and molecular reaction dynamics. The Stark deceleration technique yields unprecedented control over both the internal and external degrees of freedom of polar molecules in a molecular beam. The combination of both techniques offers new possibilities in scattering experiments. The advantages of such an approach are the control over the external and internal degrees of freedom e.g. a tunable collision energy, a narrow energy spread and a selected quantum state. We will discuss our results on the inelastic scattering of state selected $\text{OH}(X^2\Pi_{3/2}, J=3/2, f)$ radicals with hexapole state-selected $\text{NO}(X^2\Pi_{1/2}, J=1/2, f)$ radicals, as a function

of the collision energy. Excitation functions of four rotational excited channels have been measured and will be presented.

MO 16.5 Thu 11:30 V38.02

Study on the pyridine aggregation in helium nanodroplets — ●PABLO NIETO, TORSTEN POERSCHKE, DANIEL HABIG, GERHARD SCHWAAB, and MARTINA HAVENITH — Department of Physical Chemistry II, Ruhr-University, 44780 Bochum, Germany

Pyridine crystals show the unusual property of isotopic polymorphism. Experimentally it has been observed that deuterated pyridine crystals exist in two phases while pyridine does not show a phase transition [1]. Therefore, although isotopic substitution is the smallest possible modification of a molecule it greatly affects the stability of pyridine crystals. A possible experimental approach in order to understand this striking effect might be the study of pyridine aggregation for small clusters. By embedding the clusters in helium nanodroplets the aggregates can be stabilized and studied by means of Infrared Depletion Spectroscopy.

Pyridine small clusters were identified in the C-H asymmetric vibration region ($3000\text{--}3100\text{ cm}^{-1}$) using this method. The number of molecules of the clusters responsible of the different bands were identified by means of pickup curves measurements as well as mass sensitive detection of the clusters. Investigations with stark field measurements will be also discussed.

[1] S. Crawford *et al.*, *Angew. Chem. Int. Ed.*, 48, 755 (2009)

MO 16.6 Thu 11:45 V38.02

Time-Of-Flight and Velocity-Map-Imaging-Spectroscopy of Rubidium-doped Helium Nanodroplets — ●AMON SIEG¹, LUTZ FECHNER², BARBARA GRÜNER¹, MARCEL MUDRICH¹, and FRANK STIENKEMEIER¹ — ¹Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany — ²Max-Planck-Institut für Kernphysik, 69029 Heidelberg, Germany

Helium nanodroplets provide an ideal matrix for spectroscopy of embedded atoms and molecules due to the low temperature conditions (0.4 K) and extremely weak interactions with the dopants. In our experiments we ionize rubidium atoms attached to helium nanodroplets via resonant 2-photon-ionization. With our time-of-flight mass spectrometer we are able to discriminate between neat Rb^+ ions and RbHe_n^+ -exciplexes ($n=1,2$) which are formed upon excitation. The mass-resolved excitation spectra are in agreement with a pseudodiatomic model which treats the dopant atom as one and the whole helium droplet as the other atom of a diatomic molecule. From velocity-map-images (VMI) of photoelectrons and ions we extract energies and angular distributions which give detailed insight into the desorption process of excited Rb and RbHe_n off the droplets.

MO 16.7 Thu 12:00 V38.02

Photoionization dynamics of rubidium atoms attached to helium nanodroplets with amplified femtosecond laser pulses — ●BARBARA GRÜNER, MANUEL ROMETSCH, FRANK STIENKEMEIER, and MARCEL MUDRICH — Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany

Photoionization of alkali-doped helium nanodroplets with femtosecond laser pulses entails complex dynamics which strongly depends on the laser pulse intensity. Low laser intensities allow for investigating the desorption process of the alkali atom off the surface of the helium droplet and may induce exciplex formation, depending on the excitation wavelength [1,2]. At high pulse intensities the ionization of the dopant atoms induces the ignition of a nanoplasma that resonantly couples to the laser field [3]. However, this has not been studied, so far, for dopants residing at the surface of the droplets. We present first experiments on the photoionization dynamics of alkali-doped He nanodroplets using an amplified femtosecond laser.

[1] Krishnan *et al.*, *Phys. Rev. Lett.* 107, 173402 (2011)

[2] Droppelmann, *et al.* *Phys.Rev.Lett.* 93, 023402 (2004)

[3] Mudrich *et al.*, *Phys. Rev. Lett.* 100, 023401 (2008)

MO 16.8 Thu 12:15 V38.02

Investigation of Organic Molecules (PTCDA, Phthalocyanines and Porphyrines) in Helium Nanodroplets or on Neon Clusters — ●MARKUS MÜLLER, MATTHIEU DVORAK, SEBASTIAN MÜLLER, LUKAS SCHÄFER, FABIAN HOHNLOSER, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str.3, 79104 Freiburg

Organic molecules either used as organic semiconductors (PTCDA) or as dyes in organic solar cells like copper phthalocyanine (CuPc) gain high interest in their optoelectronic properties. To reveal the electronic structure of these molecules we utilize Helium Nanodroplet Isolation (HENDI) Spectroscopy, a well established method to characterize single molecules but also molecular complexes inside a cold (370 mK) and weak interacting surrounding.

Laser Induced Fluorescence (LIF) excitation and emission spectra provide insight into the vibrational structure of the electronic ground state and the first electronically excited state. We present (LIF) absorption and fluorescence emission spectra of various organic molecules and complexes of them attached to helium nanodroplets. Furthermore, measurements with neon clusters have been performed in order to study the effect of the different cryogenic environment (line shifts and line broadening).

MO 17: Femtosecond Spectroscopy IV

Time: Thursday 10:30–12:45

Location: V38.03

Invited Talk

MO 17.1 Thu 10:30 V38.03

Ultrafast Processes in Single Molecules: from Small Chromophores to Photosynthetic Antenna Complexes — ●RICHARD HILDNER¹, DAAN BRINKS¹, RICHARD J. COGDELL², and NIEK F. VAN HULST^{1,3} — ¹ICFO - Institut de Ciències Fotòniques, 08860 Castelldefels — ²University of Glasgow, Glasgow G12 8TA — ³ICREA - Institutio Catalana de Recerca i Estudis Avancats, 08015 Barcelona

Ultrafast excitation-energy transfer is at the heart of both natural and artificial light-harvesting, and plays a key role in the initial steps of photosynthesis as well as in photovoltaic applications of organic functional materials. However, a detailed nanoscale understanding of energy-transfer processes is hampered to date, because molecular systems are often highly heterogeneous with disordered environments and current ultrafast techniques intrinsically average over large ensembles.

Here, we present our recent advances in combining femtosecond pulse-shaping techniques with single-molecule detection schemes at room temperature. Employing phase-controlled double-pulse excitation, we resolved ultrafast electronic coherences and their femtosecond decay in a model system, individual terrylene molecules embedded in a polymer matrix. We also observed and manipulated vibrational wave packet interference in single molecules by adapting the time and phase distribution of the laser field to the ultrafast molecular dynamics. Finally, we discuss how these techniques can be extended to multi-chromophoric molecular systems. Preliminary results on the ultrafast

dynamics of electronic excitations within individual light-harvesting complexes of purple bacteria are presented.

MO 17.2 Thu 11:00 V38.03

Ultrafast Chromophore Dynamics in Xanthorhodopsin — ●MIRIAM COLINDRES¹, MELANIE GEIER², ILKA HAFERKAMP², EKKEHARD NEUHAUS², and ROLF DILLER¹ — ¹Physics Department, University Kaiserslautern, Germany — ²Biology Department, University Kaiserslautern, Germany

Xanthorhodopsin from the extreme halophile eubacterium *Salinibacter ruber* is one of the simplest bioenergetic systems for collecting light using excited state energy transfer. This member of the retinal protein family is a light driven transmembrane proton pump (SX) (1). We present the first results of ultrafast vibrational dynamics on a sub-ps time scale of the primary photoreaction in xanthorhodopsin. Our experiments show evidence for the proton-pump cycle initiated by Ret isomerization after excitation of SX. The Ret S_1 surface branches into the hot J-state and the hot all-trans-Ret, followed by vibrational cooling and torsional relaxation of J-state and all-trans-Ret. Our results suggest a prolonged protein response compared to bacteriorhodopsin. The protein relaxes slower than in BR (11 ps) (2) and the perturbation of protein is permanent on the experimental time scale. In this context the excited state dynamics of SX as a sensor for protein dynamics are of particular interest. Therefore we are currently investigating the vibrational modes of SX in the carbonyl region between 1700 and 1800

cm⁻¹.

- (1) J. Antón et al., IUMS, 52, 485-491 (2002)
 (2) R. Groß et al., J. Am. Chem. Soc., 131, 14868-14878 (2009)

MO 17.3 Thu 11:15 V38.03

Possible involvement of multi-photon pathways in femtosecond transient absorption experiments on retinal-isomerization in Bacteriorhodopsin — ●JAN PHILIP KRAACK, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

The photo-isomerization of all-trans retinal in Bacteriorhodopsin (BR) is an important model-reaction in time-resolved spectroscopy on rhodopsins. Upon photon-absorption, the excited-state population decays within less than a picosecond to form the ground state photoproduct with high quantum yield around 0.6. An important issue in the interpretation of BR's photo-dynamics concerns observable dependences of the signal on intensities of excitation pulses.[1-2] Using hyperspectral transient absorption spectroscopy, we investigated the femtosecond reaction kinetics of BR for a series of experimental parameters. In particular, we find that excited state relaxation dynamics depend on the excitation wavelength over a broad energetic range of excitation (500-600 nm). Screening of excitation-pulse intensities influences the ratio between ground state bleaching- and photo-product signal. The results are discussed in the context of existing two-photon pathways for the generation of photo-products not participating in the active photo-cycle of BR.[3]

[1]Floresan et al., PNAS 2009, 106, 10896. [2]Prokhorenko et al., J.Chem. Phys. 2011, 134, 085105. [3]Fischer et al. Biophys., J. 2005, 89, 1175.

MO 17.4 Thu 11:30 V38.03

Energy Transfer in Light-Harvesting Systems: Influence of Non-Markovian Environment — ●GERHARD RITSCHEL¹, JAN RODEN², WALTER T. STRUNZ³, and ALEXANDER EISFELD⁴ — ¹Max-Planck-Institut für Physik komplexer Systeme, Dresden, Germany — ²University of California, Berkeley, USA — ³Technische Universität Dresden, Germany — ⁴Harvard University, Cambridge, USA

The transfer of electronic excitation energy as well as optical properties of complexes of interacting chromophores, e.g. the FMO complex or the LH2 antennae in biological photosynthetic systems, are strongly influenced by an environment. For a proper theoretical description it is essential to include non-Markovian effects resulting from an electron-environment coupling that is a rather structured function of energy leading to a complicated retroaction on the excitation dynamics.

We developed a new approach based on non-Markovian quantum state diffusion [1] where it is possible to efficiently calculate energy transfer and optical spectra in a non-perturbative way. Within this method, it is possible to capture the whole range from coherent dynamics to incoherent diffusion and to investigate situations where environment-assisted transfer occurs.

Using that approach we described the energy transfer dynamics in one FMO subunit as well as in the full FMO trimer [2, 3] and calculated linear spectra at various temperatures.

- [1] Roden et al. PRL 103, 058301 (2009)
 [2] Ritschel et al. NJP 13, 113034 (2011)
 [3] Ritschel et al. JPCL 2, 2912 (2011)

MO 17.5 Thu 11:45 V38.03

Ultrafast Electronic Deactivation Dynamics of the Rare Natural Nucleobases Xanthine and Hypoxanthine — ●KATHARINA RÖTTGER and FRIEDRICH TEMPS — Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Olshausenstr. 40, D 24098 Kiel, Germany

Investigations of the photophysical behaviour of rare DNA and RNA bases provide insight into the correlation between structural properties of the nucleobases and their radiationless decay pathways after UV excitation. Here, we report on the first femtosecond time-resolved transient absorption measurements of the rare RNA nucleotide xanthosine monophosphate in buffered aqueous solution at different pH values and on the rare natural RNA base hypoxanthine. Measurements were performed with a transient absorption setup which allows for a highly sensitive, simultaneous detection of broadband absorption spectra (300-700 nm) and single-colour absorption in the deep UV range. The excited-state dynamics of xanthosine monophosphate (XMP) have been found to depend strongly on the excitation wavelength. It was possible to *distinguish* the dynamics of two close lying

$\pi\pi^*$ states which are most likely connected via a conical intersection. The direct observation of the consecutive population of these states is quite rare in the case of the nucleobases. The dynamics of hypoxanthine were found to be similar to those of guanine. The results are discussed in comparison with recently published computational studies on possible relaxation channels.

MO 17.6 Thu 12:00 V38.03

Ultrafast dynamics of NH stretch vibrations in adenosine-thymidine base pairs in chloroform solution — ●CHRISTIAN GREVE¹, BENJAMIN KOEPE¹, HENK FIDDER¹, NICHOLAS PREKETES³, ERIK T. J. NIBBERING¹, SHAUL MUKAMEL³, FRIEDRICH TEMPS², and THOMAS ELSAESSER¹ — ¹Max Born Institut für Nicht-lineare Optik und Kurzzeitspektroskopie, Max Born Strasse 2A, 12489 Berlin, Germany — ²Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Olshausenstr. 40, 24098 Kiel, Germany — ³Department of Chemistry, University of California, Irvine, USA

The nucleobases adenine (A) and thymine (T), building blocks in native DNA and RNA, readily form hydrogen bonded complexes both in the gas phase and in solution. To gather key insight into these hydrogen bonding interactions, we perform femtosecond IR-pump-IR-probe and polarization-resolved 2D-IR photon echo spectroscopy of the N-H stretching bands of AT base pairs in chloroform solution which are located between 3100 and 3500 cm⁻¹. Vibrational population dynamics of hydrogen bonded stretch transitions occur on a subpicosecond time scale. Cross peaks in the 2D-IR spectra, monitored as a function of waiting time, show the connectivities in the N-H stretching manifold. The polarization dependence of the cross peaks indicate that the hydrogen-bonded and the free N-H stretching dipole moments in these AT base pairs have a well-defined relative orientation. Our experimental results are combined with quantum chemical calculations to allow for N-H stretching mode assignments of the Watson-Crick and Hoogsteen base pair structural motifs present in solution.

MO 17.7 Thu 12:15 V38.03

Time-resolved spectroscopy of triplet states of thymidylic acids — ●BERT MANUEL PILLES — LMU Munich

Solar UV radiation is known to induce harmful mutagenic products in DNA. The major photoproduct is the cyclobutane pyrimidine dimer (CPD) between neighboring thymine residues. In recent studies it was shown that the photodimerization reaction induced via 266 nm excitation occurs predominantly on a 1 ps time scale. This finding suggests that the reaction occurs via a singlet pathway [1,2]. Nevertheless triplet states are discussed to be possible precursors of thymine dimer formation.

We used time resolved UV pump, IR probe spectroscopy - covering picoseconds to microseconds - to investigate different single stranded thymidylic acids (TpT, (dT)18) and the corresponding mononucleotide (thymidine monophosphate, TMP). We show that femtosecond infrared spectroscopy can address triplet specific bands and that the excitation of the samples leads to the formation of triplet states that decay on the ns time scale. Different quenching mechanisms (CPD formation, self quenching, oxygen quenching) will be discussed.

[1]: Schreier, W. J., J. Kubon, et al. (2009). "Thymine Dimerization in DNA Model Systems: Cyclobutane Photolesion Is Predominantly Formed via the Singlet Channel." Journal of the American Chemical Society 131(14): 5038-5039.

[2]: Schreier, W. J., T. E. Schrader, et al. (2007). "Thymine dimerization in DNA is an ultrafast photoreaction." Science 315(5812): 625-629.

MO 17.8 Thu 12:30 V38.03

Excited state dynamics and binding energies of DNA bases in aqueous solution — ●FRANZISKA BUCHNER and ANDREA LÜBCKE — Max-Born-Institut, Max-Born-Strasse 2A, 12489 Berlin, Germany

Interaction of UV light with DNA may lead to photodamage. Photodamage of DNA can occur either by direct absorption of uv photons or by attachment of solvated electrons formed by a photodetachment process in the vicinity.

We report on the excited state dynamics of DNA bases in aqueous solution observed by time-resolved photoelectron spectroscopy, exploiting the liquid jet technique. Sub-100 fs pulses of 200 nm or in the range of 240-266 nm are used to excite a 1 mmolar solution of the DNA base or its sugar conjugate. Excited state dynamics is probed by photoionization with a delayed UV pulse (also sub-100 fs).

Depending on the photon energy of the pump pulse we either see formation and recombination of solvated electrons or excited state dy-

namics of the base itself. Both population dynamics and binding en-

ergies of the excited states will be discussed.

MO 18: Molecular Dynamics

Time: Thursday 14:00–16:00

Location: V38.02

Invited Talk

MO 18.1 Thu 14:00 V38.02

Excited-states and nonadiabatic dynamics: unveiling mechanistic aspects of ultrafast photoprocesses in nucleobases — ●MARIO BARBATTI — Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany

After UV excitation, all five natural nucleobases composing our genetic code return to ground state without photon emission in the time scale of 1 ps. This ultrafast deactivation, which increases the photostability of the nucleobases, may have been one of the factors contributing to their selection among a number of other possibilities in early biotic history on Earth. In the last years, theoretical simulations along with time-dependent spectroscopy have worked to determine the excited-state mechanisms employed by these molecules in their ultrafast deactivation. In particular, semi-classical nonadiabatic dynamics simulations have revealed a complex scenario, where multiple different reaction pathways are in constant competition between them [1] and whose output is deeply dependent on details of potential-energy surfaces of each nucleobases [2]. In this contribution, the current state of this topic is reviewed and the strengths and limitations of the available theoretical methods to deal with these phenomena are critically appraised.

[1] M. Barbatti, A. J. A. Aquino, J. J. Szymczak, D. Nachtigallová, P. Hobza, and H. Lischka, *Proc. Natl. Acad. Sci. U. S. A.* **107**, 21453 (2010).

[2] M. Barbatti and S. Ullrich, *Phys. Chem. Chem. Phys.* **13**, 15492 (2011).

MO 18.2 Thu 14:30 V38.02

Improvements to the Instanton Method: Tunneling in Large Systems — ●JUDITH B. ROMMEL and JOHANNES KÄSTNER — Institute of Theoretical Chemistry, University of Stuttgart, Germany

Quantum tunneling of atoms has a major impact on chemical reactions, in particular on reactions including hydrogen transfers. The enzyme glutamate mutase catalyzes a radical reaction involving two hydrogen transfers. We found the hydrogen transfers to be rate limiting [1]. The experimentally found kinetic isotope effects ranging from 6 to 30 suggest hydrogen tunneling. An improved path-integral-based instanton approach is used to figure out how the enzyme modulates these effects. The calculation of tunneling rates and kinetic isotope effects in systems with several hundred degrees of freedom like enzymes requires to locate the instanton via an optimization. We found a quadratically converging Newton-Raphson method to be better than mode following methods. The tangent mode method, recently proposed by us, turned out to be the fall-back option [2]. A variable step size formulation of the instanton rate theory allows to distribute sampling points more evenly along the bounce. Therefore, less sampling points are necessary which significantly reduces the computational effort [3].

[1] J.B. Rommel, J. Kästner, *J. Am. Chem. Soc.*, **133**, 10195, 2011.

[2] J.B. Rommel, T.P.M. Goumans, J. Kästner, *J. Chem. Theory Comput.*, **7**, 690, 2011.

[3] J.B. Rommel, J. Kästner, *J. Chem. Phys.*, **134**, 84107, 2011.

MO 18.3 Thu 14:45 V38.02

Fragmentation of the protonated water dimer via non-adiabatic pathways after valence photoionization — ●ZHENG LI¹, ORIOL VENDRELL¹, and ROBIN SANTRA^{1,2} — ¹CFEL, DESY, Notkestr. 85, D-22607 Hamburg, Germany — ²Department of Physics, University of Hamburg, D-20355 Hamburg, Germany

The protonated water dimer, (H₂O)-H⁺-(H₂O), irradiated with the free-electron laser FLASH at DESY (90 eV), undergoes Coulomb-explosion after losing one of its valence electrons via photoionization[1]. The diversity of valence orbitals available for ionization and the large mobility of the central proton lead to increased complexity of its dynamics. The strong two-body dissociation channel H₅O₂⁺ → H₃O⁺ + H₂O⁺ + e⁻ prevails, yet fragmentation channels involving H⁺ and neutral fragments need to be experimentally identified. Because of the closely-lying outer valence orbitals and various conical intersections, non-adiabatic effects are presumably im-

portant for the overall dynamics. *Ab initio* potential energy surfaces for the three lowest dicationic states have been computed at the CASSCF(8,11)//Koopmans level. A regularized diabaticization scheme has been used to obtain a diabatic representation of the Hamiltonian[2]. The quantum dynamics of the photofragmentation has been investigated using the multi-configuration time-dependent Hartree (MCTDH) method[3], the results unravel the underlying mechanism.

[1] L. Lammich *et al.*, *Phys. Rev. Lett.* **105**, 253003 (2010). [2] H. Koeppel *et al.*, *J. Chem. Phys.* **115**, 2377 (2001). [3] M. H. Beck *et al.*, *Physics Reports* **324**, 1 (2000).

MO 18.4 Thu 15:00 V38.02

Ultrafast Dynamics of Photoionized molecules — MOHAMED EL-AMINE MADJET¹, ORIOL VENDRELL¹, and ●ROBIN SANTRA^{1,2} — ¹Center for Free-Electron Laser Science, DESY, Germany — ²Department of Physics, University of Hamburg, Germany

Using a mixed quantum-classical approach, we investigated theoretically the dynamics of acetylene and ethylene after extreme ultraviolet (XUV) photoionization. For acetylene cations produced in the A²Σ_g⁺, we show that the decay of this state occurs via both ultrafast isomerization and non-radiative electronic relaxation [M.E.M. *et al.*, *Phys. Rev. Lett.*, in print (2011)]. We find a time-scale for hydrogen migration and electronic decay of about 60 fs, in good agreement with recent XUV-pump/XUV-probe time-resolved experiments on the same system [Y.H. Jiang, *et al.* *Phys. Rev. Lett.* **105**, 263002(2010)]. Moreover, we predict an efficient vibrational energy redistribution mechanism that quickly transfers excess energy from the isomerization coordinates to slower modes in a few hundred femtoseconds, leading to a partial regeneration of acetylene-like configurations. Preliminary results for ethylene cations will also be presented and discussed.

MO 18.5 Thu 15:15 V38.02

Multi reference perturbation theory for non-adiabatic on-the-fly molecular dynamics: implementation and benchmarking — ●SVEN OESTERLING, ARTUR NENOV, BENJAMIN P. FINGERHUT, and REGINA DE VIVIE-RIEDLE — Ludwig Maximilians Universität München, Department Chemie

Semiclassical on-the-fly dynamics provide a way to simulate molecular processes of moderate sized systems. Treating the nuclei classically, abolishes the need to precompute potential energy surfaces, and thus allows for a full dimensional treatment of the molecular degrees of freedom. The electronic properties are computed with quantum chemical methods, adequate for system-size and nature of the problem. Regarding excited states, major challenges are the accurate, yet cost efficient calculation of the electron correlation, and the precise description of non-adiabatic events. The complete active space perturbation theory (CASPT2) has been shown to resolve the correlation issue, yielding excitation energies close to experimental values.

We implemented an interface for the CASPT2 method, included in the Molpro quantum chemistry package, in the Newton-X dynamics package. As there are no analytical non-adiabatic coupling vectors available in common quantum chemistry programs, a numerical approach, suggested by Tao *et al.*, was used to compute the coupling. The implementation is benchmarked with ethylene, with additional focus on the relevance of Rydberg-states.

MO 18.6 Thu 15:30 V38.02

Surface hopping from accurate quantum-classical correspondence — ●SEBASTIAN MÖBIUS¹, SEBASTIAN WÜSTER¹, MILAN SINDELKA¹, ALEXANDER EISFELD^{1,2}, and JAN MICHEAL ROST¹ — ¹Max Planck Institute for physics of complex systems, Dresden, Germany — ²Department for Chemistry and Chemical Biology, Harvard University, Boston, USA

Mixed quantum-classical treatments of molecular dynamics are well established to study chemical reaction pathways or collision dynamics. The main idea is to evolve nuclear coordinates on classical trajectories, governed by Newton's equation of motion, and the electronic degrees of freedom fully quantum mechanical by Schroedinger's equation.

In contrast to Ehrenfest methods, Tully presented a multi-trajectory surface hopping algorithm, which allows for non-adiabatic transitions between adiabatic eigenstates. This algorithm has been proven successful in various cases, studying collision dynamics. While the traditional derivation of the method arguably gives rise to only part of the non-adiabatic coupling terms in the Born-Oppenheimer separated Schroedinger equation, we present a more sophisticated approach which can reproduce all couplings. Our crucial argument is that only hermitian operators ought to be replaced with a classical variable. We discuss model systems where the newly introduced terms are required in order to match the full quantum calculations. Our extensions of Tully's algorithm opens up new possibilities of application, like spin-orbit coupled systems, atomic Rydberg systems and multidimensional surface intersections (e.g conical intersections).

MO 18.7 Thu 15:45 V38.02

Semiclassical Wigner propagation as a numerical tool in molecular dynamics — ●SERGEI D. IVANOV^{1,2}, THOMAS DITTRICH³, and DOMINIK MARX¹ — ¹Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Bochum, Germany — ²Present address: Quantum Dynamics Group, Institut für Physik, Universität

Rostock, Rostock, Germany — ³Departamento de Física, Universidad Nacional de Colombia, Bogotá D.C., Colombia

The Wigner function constitutes a one-to-one representation of the quantum mechanical density operator, including coherences. The state-of-the-art methods based on LSC-IVR readily reproduce static quantum effects already present in the initial state, whereas truly dynamical quantum effects that arise during the time evolution in the presence of nonlinear potentials remain outside reach. Major progress could be achieved through the insight that even quantum coherences can be time-evolved faithfully if the propagation is not based on single but on *pairs* of classical trajectories [1]. Here, we attempt to make an important step ahead towards employing semiclassical Wigner propagation in the molecular dynamics framework; that is to recast the successful grid-based formulation in [2,3] well-suited for low-dimensional problems, into a grid-free representation where all relevant dynamical quantities are evaluated directly as averages over trajectory ensembles.

[1] P. P. de M. Rios and A. M. Ozorio de Almeida., *J. Phys. A: Math. Gen.*, 35:2609, 2002. [2] T. Dittrich and L. A. Pachón., *Phys. Rev. Lett.*, 102:150401, 2009. [3] T. Dittrich, E. Gómez, and L. A. Pachón., *J. Chem. Phys.*, 132:214102, 2010

MO 19: Cold Molecules II

Time: Thursday 14:00–16:00

Location: V38.03

Group Report

MO 19.1 Thu 14:00 V38.03

Sisyphus Cooling of Polyatomic Molecules — ●MARTIN ZEPPENFELD, BARBARA G.U. ENGLERT, ROSA GLÖCKNER, MANUEL MIELENZ, CHRISTIAN SOMMER, LAURENS VAN BUUREN, MICHAEL MOTSCH, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching, Germany

Interest in ultracold polar molecules has experienced tremendous growth in recent years, with potential applications reaching beyond those of ultracold atoms due to additional internal degrees of freedom and long-range dipole-dipole interactions. Developing methods to prepare the required ensembles of ultracold molecules has been a formidable challenge. To this end, we have now achieved first results with opto-electrical cooling [1], a general Sisyphus-type cooling scheme for polar molecules. Molecules are cooled by more than a factor of 4 with an increase in phase space density by a factor of 7. This achievement is based on the combination of two developments. First, a completely new type of electric trap allows molecules to be confined in predominantly homogeneous fields for 10s of seconds [2]. Second, the combination of mm-wave radiation with a narrow-band mid-infrared laser allows optical pumping among a closed set of rotational and vibrational molecular states. Improvements will allow cooling of molecules to Mikrokkelvin temperatures in the near future, opening a route to experiments with molecular quantum-degenerate gases.

[1] M. Zeppenfeld *et al.*, *Phys. Rev. A* **31**, 365 (2004)
[2] B.G.U. Englert *et al.*, *Phys. Rev. Lett.*, in press(arXiv:1107.2821)

MO 19.2 Thu 14:30 V38.03

A Centrifuge Molecular Decelerator for Polar Molecules — ●SOTIR CHERVENKOV, XING WU, ANDREAS ROHLFES, JOSEPH BAYERL, LAURENS D. VAN BUUREN, CHRISTIAN SOMMER, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Straße 1, 85748 Garching bei München

We present a novel technique for deceleration of neutral polar molecules, which employs the centrifugal potential in a rotating frame. The idea is to inject and electrically guide [1] a dense continuous beam of polar molecules from the periphery to the center of the rotating frame along a spiral trajectory. Thus the molecules climb up a centrifugal potential hill and get decelerated as they propagate. Since the rotational speed is tunable, the centrifuge decelerator is well-suited for a large range of input velocities. Moreover, in combination with our cryogenic source [2], internally cold molecules will be decelerated. For this setup, simulations show that ammonia beams with velocities below 20 m/s and with fluxes of 10⁹ molecules/s are feasible. The outgoing quasi-continuous, slow, and dense molecular beams are ideal for various applications requiring cold molecules, in particular, for trapping and subsequent opto-electrical cooling [3].

[1] S.A. Rangwala *et al.*, *Phys. Rev. A* **67**, 043406 (2003)
[2] L.D. van Buuren *et al.*, *Phys. Rev. Lett.* **102**, 033001 (2009)
C. Sommer *et al.*, *Faraday Discuss.* **142**, 203 (2009)

[3] M. Zeppenfeld *et al.*, *Phys. Rev. A* **80**, 041401 (2009),

MO 19.3 Thu 14:45 V38.03

Guided continuous supersonic beams of polar molecules from a cryogenic buffer-gas source — ●XING WU, CHRISTIAN SOMMER, SOTIR CHERVENKOV, ANDREAS ROHLFES, MARTIN ZEPPENFELD, LAURENS VAN BUUREN, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, D-85748 Garching, Germany

In order to obtain dense samples of internally and translationally cold polar molecules, we use the method of buffer-gas cooling [1], combined with supersonic expansion. We have demonstrated that when the cryogenic buffer-gas cell is operated in a supersonic regime, molecular fluxes are hydrodynamically enhanced by up to two orders of magnitude. Meanwhile, the translational velocity profile of the output molecular beam is cooled to beyond Mach number 6 via supersonic expansion. Due to the cryogenic cell temperature, the forward velocity of the supersonic molecular beam is below 190 m/s. The low-field-seeking molecules in the so-produced continuous supersonic beam are selected via quadrupole electric guiding and transferred to further experiments. Such high-flux guided continuous supersonic beams from a cryogenic reservoir provide a promising source of polar molecules amenable to deceleration and further cooling.

[1] C. Sommer *et al.*, *Faraday Discussions* **142**, 203 (2009)
L.D. van Buuren *et al.*, *Phys. Rev. Lett.* **102**, 033001 (2009)

MO 19.4 Thu 15:00 V38.03

A microwave decelerator for polar molecules — ●SIMON MERZ¹, NICOLAS VANHAECKE¹, WOLFGANG JÄGER², MELANIE SCHNELL³, and GERARD MEIJER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin — ²University of Alberta, Edmonton, Canada — ³Center for Free Electron Laser Science, D-22607 Hamburg

An important remaining issue in the field of cold molecules is a general technique to manipulate the motion of polar molecules in high-field-seeking states, which is crucial for the investigation of molecules in their ground states and of all large and more complex molecules. In contrast to the already demonstrated and experimentally rather challenging alternating gradient methods, we exploit the interaction of polar molecules with electromagnetic radiation in a microwave cavity. Based on the concept of our microwave lens [1] we have developed a decelerator for polar molecules, that allows motion control in 3D. We will present a detailed characterisation of the microwave decelerator, e.g. its phase-space acceptance, and discuss prospects for future experiments.

[1] H. Odashima *et al.* *Microwave Lens for Polar Molecules.* *Phys. Rev. Lett.*, 104:253001, 2010

MO 19.5 Thu 15:15 V38.03

A traveling-wave Zeeman decelerator — ●DONGDONG ZHANG¹, JEAN-PAUL CROMIÈRES², HENRIK HAAK¹, GERARD MEIJER¹, and

NICOLAS VANHAECKE¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²Laboratoire Aimé Cotton, CNRS, Université Paris-Sud, 91405 Orsay, France

A prominent, versatile method to produce cold molecules relies on the supersonic expansion of a seeded molecular gas, followed by a deceleration of the molecules of the so-formed beam. While Stark deceleration allows one to manipulate the longitudinal motion of polar molecules of a supersonic beam with time-dependent, inhomogeneous electric fields, Zeeman deceleration uses time-dependent, inhomogeneous magnetic fields to control the motion of paramagnetic molecules [1]. Here we report on an approach to the magnetic deceleration of supersonic beams, based on the generation of a propagating wave of magnetic field [2]. The fields provide real-time tri-dimensional confinement of the particles in low-field-seeking states, in analogy with the traveling-wave Stark decelerator [3]. Our Zeeman decelerator avoids losses of molecules even at low forward velocities, prevents non-adiabatic transitions, and ideally matches a static magnetic trap.

[1] N. Vanhaecke, U. Meier, M. Andrist, B. H. Meier, and F. Merkt, *Phys. Rev. A* **75**, 031402(R) (2007).

[2] A. Trimeche, M. N. Bera, J.-P. Cromières, J. Robert, and N. Vanhaecke, *Eur. Phys. J. D*, **65**, 263 (2011).

[3] A. Osterwalder, S. A. Meek, G. Hammer, H. Haak, and G. Meijer, *Phys. Rev. A* **81**, 051401(R) (2010)

MO 19.6 Thu 15:30 V38.03

Multistage Zeeman deceleration of paramagnetic atoms and molecules — ●MICHAEL MOTSCH, ALEX W. WIEDERKEHR, STEPHEN D. HOGAN, and FRÉDÉRIC MERKT — Laboratorium für Physikalische Chemie, ETH Zürich, CH-8093, Switzerland

In a multistage Zeeman decelerator, time-dependent, inhomogeneous magnetic fields are applied to control the velocity of supersonic beams of paramagnetic atoms and molecules. Using an array of 91 de-

celeration solenoids, we have produced velocity-controlled beams of metastable neon atoms at translational temperatures as low as 10 mK in the comoving frame of reference and characterized the phase-space acceptance of the multistage Zeeman decelerator. By applying deceleration pulse sequences for different isotopes of neon, we have investigated the selectivity of the deceleration process on the magnetic-moment-to-mass ratio of the particles in the beam [1]. The versatility of the method is demonstrated by producing slow beams of oxygen molecules in the $X^3\Sigma_g^-$ electronic ground state, which enables the study of internal-state selectivity in the deceleration process.

[1] A. W. Wiederkehr et al., *J. Chem. Phys.* **135**, 214202 (2011).

MO 19.7 Thu 15:45 V38.03

A Stern-Gerlach Slower — ●ULRICH KROHN, ARIN MIZOURI, KATHERINE HORNE, JAMES ALMOND, and DAVID CARTY — Durham University, Physics Department, Durham DH1 3LE

We study a modified design of a magnetic conveyor decelerator [1] that should enable us to slow down a very large number of molecules of various species. The project aims to create polar molecules with sufficient density and low enough temperature that they can form interacting quantum arrays. As an instrument this be used as a quantum simulator - an ideal, tuneable and highly versatile tool for modelling strongly-interacting quantum systems and understanding the remarkable quantum phenomena they exhibit.

The presented Stern-Gerlach slower will be the first step to slow molecules from their initial velocities to almost standstill in order to load it into a magnetic trap and sympathetically cool them to even lower temperatures using a cloud of ultracold atoms.

References

- [1] A Trimeche, *et al.*, *European Physical Journal D*. **65**, 263 (2011)
 [2] E Lavert-Ofir, *et al.*, *Phys. Chem. Chem. Phys.* **13**, 18948 (2011)
 [3] E A Hinds, I G Hughes, *J. Phys. D: Appl. Phys.* **32**, R119 (1999)

MO 20: Atomic clusters (with A)

Time: Thursday 14:00–16:00

Location: V57.05

Invited Talk

MO 20.1 Thu 14:00 V57.05

X-ray magnetic circular dichroism spectroscopy of size-selected free cluster ions: spin coupling, orbital angular momentum quenching, and magnetic dopants — ●TOBIAS LAU — Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institut für Methoden und Instrumentierung der Forschung mit Synchrotronstrahlung, Albert-Einstein-Straße 15, 12489 Berlin

X-ray magnetic circular dichroism (XMCD) spectroscopy is a local and element specific probe to study spin and orbit contributions to the total magnetic moment. With a 5 T and 15 K linear ion trap setup we have successfully applied XMCD of size selected cluster ions to study fundamental magnetic properties of transition metals in the molecular limit. Recent results include the observation of ferromagnetic spin coupling in small clusters of archetypical bulk antiferromagnets, as well as antiferromagnetic spin coupling in iron, the most typical 3d bulk ferromagnet. We could also show that the orbital angular momentum is largely quenched already for the smallest iron clusters. Furthermore, magnetization curves recorded at fixed ion trap temperature can be used to determine the cluster ion temperature. As an outlook, first results of XMCD spectroscopy of single impurity atoms in size selected clusters ions will be presented.

Invited Talk

MO 20.2 Thu 14:30 V57.05

Autoionization of clusters: Energy transfer vs. electron transfer — ●UWE HERGENHAHN — Max-Planck-Institut für Plasmaphysik, EURATOM Association, 85748 Garching

In this talk I will give a progress report about our experimental work on autoionization of clusters. The discovery of autoionizing decays into charge separated two-hole sites in clusters (Interatomic/Intermolecular Coulombic Decay, ICD) has been followed by experiments, in which such decays are mediated by charge transfer between sites (Electron Transfer Mediated Decay, ETMD). For ICD, which proceeds by energy transfer, evidence for the occurrence of this process as a second step in a cascade after normal Auger decay of water clusters will be presented. For ETMD, the interpretation of outer valence and electron-electron coincidence spectra allows to get a comprehensive picture of this au-

toionization channel in ArXe clusters of varying size.

MO 20.3 Thu 15:00 V57.05

First-order corrections and structural information in semiclassical Gaussian approximations to the Boltzmann operator for clusters of atoms — ●HOLGER CARTARIUS¹ and ELI POLLAK² — ¹Institut für Theoretische Physik, Universität Stuttgart, 70550 Stuttgart, Germany — ²Chemical Physics Department, Weizmann Institute of Science, 76100 Rehovot, Israel

Gaussian approximations to the Boltzmann operator have proven themselves in recent years as useful tools for the study of the thermodynamic properties of rare gas clusters. They are, however, not necessarily correct at very low temperatures. We introduce a numerically cheap frozen Gaussian approximation to the imaginary time propagator with a width matrix especially suited for the dynamics of clusters [1] and investigate its first-order correction to diagnose the quality of the approximation [2]. The strength of the correction to the Gaussian partition function monitored as a function of the temperature indicates that the results of the Gaussian propagator become questionable below a certain temperature, however, thermodynamic phenomena such as structural transformations occur in a temperature range for which the Gaussian approximation is predicted to be accurate.

To study transformations or dissociation effects of rare gas clusters for increasing temperature information about the structure is essential. We show how structural information can be extracted from the Gaussian imaginary time propagator.

- [1] H. Cartarius, E. Pollak, *J. Chem. Phys.* **134**, 044107 (2011)
 [2] H. Cartarius, E. Pollak, *Chem. Phys.*, in press (2011)

MO 20.4 Thu 15:15 V57.05

Core-level photoelectron spectroscopy on free mass-selected Gold clusters at the free-electron laser FLASH — ●PATRICE OELSSNER¹, JENS BAHN¹, MICHAEL KÖTHER¹, CHRISTIAN BRAUN², VOLKMAR SENZ¹, STEFFEN PALUTKE³, MICHAEL MARTINS³, GERD GANTEFÖR², BERND VON ISSENDORFF⁴, JOSEF TIGGESBÄUMKER¹, and KARL-HEINZ MEIWES-BROER¹ — ¹IfPh, Uni-Rostock — ²FB Physik, Uni-Konstanz — ³IfExp. Physik, Uni Hamburg — ⁴Fak. f. Physik,

Uni Freiburg

A promising method to investigate the electronic structure of clusters is core-level photoelectron spectroscopy as used extensively in surface science [Phys. Rev. Lett. 102, 138303 (2009)]. The VUV free electron laser FLASH at DESY delivers intense light with a wavelength down to 4.8 nm (258 eV) to allow such studies. With a hemispherical analyzer equipped with a Delay-Line-Detector we studied core-level-binding energies. Results on mass-selected gold clusters anions from 45 to 150 atoms show a size-dependent 4f core-level shift as predicted by the metal sphere model [Phys. Rev. B 50,5744 (1994)]. By measuring the gold 4f binding energies of anions and cations as a function of cluster-size one can calculate, e.g. the chemical potential.

MO 20.5 Thu 15:30 V57.05

Core level photoelectron spectroscopy on free mass-selected lead clusters at FLASH — ●JENS BAHN¹, PATRICE OELSSNER¹, MICHAEL KÖTHER¹, CHRISTIAN BRAUN³, VOLKMAR SENZ², STEFFEN PALUTKE⁴, BERND VON ISSENDORFF⁵, GERD GANTEFÖR³, MICHAEL MARTINS⁴, JOSEF TIGGESBÄUMKER¹, and KARL-HEINZ MEIWES-BROER¹ — ¹Institut für Physik, Universität Rostock — ²Institut für Biomedizinische Technik, Universität Rostock — ³Fachbereich Physik, Universität Konstanz — ⁴Institut für Experimentalphysik, Universität Hamburg — ⁵Fakultät für Physik, Universität Freiburg

The electronic structure forms the basis for understanding the physical and chemical properties of clusters. A promising method to study this issue is core-level photoelectron spectroscopy using the VUV free electron laser FLASH at DESY providing wavelengths down to 4.8 nm. Results on lead clusters feature size-dependent 5d and 4f core-level shifts and reveal a remarkable change of final state screening conditions due to a metal to nonmetal transition at cluster sizes about 20 atoms [Phys. Rev. Lett. 102, 138303 (2009)]. In recent experiments a hemispherical electron spectrometer has been utilized. It became pos-

sible to allocate electron signals to each micro pulse of FLASH with a time-resolved delay-line-detector. A sequence of cluster sizes can be probed by this approach. By study of 4f core-level of lead clusters the change of the gaussian line shape to a Doniach-Sunjic profile has been observed as function of size. The evolution of the line profiles can be understood as scattering processes in finite systems.

MO 20.6 Thu 15:45 V57.05

Spin Coupling and Orbital Momentum Quenching in Small Iron and Cobalt Clusters — ●ANDREAS LANGENBERG^{1,2}, KONSTANTIN HIRSCH^{1,2}, VICENTE ZAMUDIO-BAYER^{1,2}, MARKUS NIEMEYER^{1,2}, ARKADIUSZ LAWICKI², MARLENE VOGEL², KAZUHIRO EGASHIRA³, THOMAS MÖLLER², AKIRA TERASAKI³, BERND VON ISSENDORFF⁴, and TOBIAS LAU¹ — ¹Helmholtz-Zentrum Berlin für Materialien und Energie, Albert Einstein Str. 15, 12489 Berlin — ²Technische Universität Berlin, Hardenbergstraße 36, 10623 Berlin — ³Cluster Research Laboratory, Toyota Technological Institute, Ichikawa 272-0001, Japan — ⁴Universität Freiburg, Fakultät für Physik, 79104 Freiburg, Germany

X-ray magnetic circular dichroism (XMCD) spectroscopy was performed on free and size selected iron and cobalt clusters in a linear penning trap giving direct access to spin and orbital resolved magnetic moments (m_s, m_l). For iron clusters a quenching of the orbital magnetic moments for already very small clustersizes and an antiferromagnetic coupling of Fe_{13}^+ [1] can be observed. Moreover the measured total magnetic moments of the clusters ($m_j = m_l + m_s$) are in good agreement with results from Stern-Gerlach experiments [2,3]. High resolution XMCD spectra as well as magnetization curves of cobalt and iron clusters will be discussed in detail.

[1] P. Bobadova-Parvanova, K. A. Jackson et.al., Phys. Rev. B 66, 195402 (2002)

[2] X. Xu, S. Yin et.al., Phys. Rev. Lett. 95, 237209 (2005)

[3] M. Knickelbein, Chem. Phys. Lett. 353, 221-225 (2002)

MO 21: Poster 3: Cluster, Collisions, Energy Transfer, Photochemistry, Spectroscopy in He-Droplets

Time: Thursday 16:30–19:00

Location: Poster.IV

MO 21.1 Thu 16:30 Poster.IV

Isomer-Selective IR/IR Double Resonance Spectroscopy: Isolating the Spectral Signatures of $H^+(H_2O)_6^+$ Isomers — ●NADJA HEINE¹, GIEL BERDEN², GERARD MEIJER¹, and KNUT ASMIS¹ — ¹Fritz-Haber-Institut, 14195 Berlin, Germany — ²FOM Institute, 3439 Nieuwegein, The Netherlands

Understanding how protons are hydrated remains an important and challenging research area. The anomalously high proton mobility of water can be explained by a periodic isomerization between the Eigen and Zundel binding motifs, $H_3O^+(aq)$ and $H_5O_2^+(aq)$, respectively, even though the detailed mechanism is considerably more complex. These rapidly interconverting structures from the condensed phase can be stabilized, isolated and studied in the gas phase in the form of protonated water clusters. The smallest protonated water clusters that exhibits structural isomers related to the Eigen and Zundel motifs experimentally is the protonated water hexamer $H^+(H_2O)_6^+$.

Here, we present first results on infrared/infrared (IR/IR) double resonance experiments on $H^+(H_2O)_6^+$. Protonated water clusters are formed by electrospray ionization, mass-selected, cooled to cryogenic temperatures, and messenger-tagged (H_2) in a buffer gas filled ion trap. Isomer-selective IR/IR photodissociation spectra are measured from 300-4000 cm^{-1} by combining population-labeling double resonance spectroscopy with the widely tunable IR radiation of the free electron laser FELIX. The results demonstrate that two isomers, an Eigen and a Zundel-type isomer, are indeed present and that their IR spectra can be measured individually over the complete spectral range.

MO 21.2 Thu 16:30 Poster.IV

Structural Variability in Transition Metal Oxide Clusters: Gas Phase Vibrational Spectroscopy of $V_3O_{6-8}^+$ — ●CLAUDIA BRIEGER¹, TORSTEN WENDE¹, JENS DÖBLER², ANDRZEJ NIEDZIELA², JOACHIM SAUER², GERARD MEIJER¹, and KNUT R. ASMIS¹ — ¹Fritz-Haber Institut der MPG, Berlin — ²Humboldt Universität Berlin

Vanadium oxides exhibit a high structural variability and redox activity which comes to play into heterogeneous catalysis. Interestingly,

the structure of the active sites in vanadium oxide catalysts is often not well known. Infrared photodissociation (IRPD) spectroscopy can be used to obtain structural information on isolated clusters in the gas phase. Here, we study the structures of tri-nuclear vanadium oxide cations. IRPD spectra of $V_3O_6^+He_{1-4}$, $V_3O_7^+Ar_{0-1}$, and $V_3O_8^+Ar_{0-2}$ from 350 to 1200 cm^{-1} are presented. $V_3O_7^+$ and $V_3O_8^+$ have a cage-like structure whereas a chain isomer is found to be most stable for $V_3O_6^+$. The binding of the rare gas atoms to $V_3O_{6-8}^+$ clusters is found to be strong, up to 58 kJ/mol for Ar, and markedly isomer-dependent, resulting in two interesting effects. First, for $V_3O_7^+Ar_1$ and $V_3O_8^+Ar_1$ an energetic reordering of the isomers compared to the bare ion is observed, making the ring-motif the most stable one. Second, different isomers bind different number of rare gas atoms. We demonstrate, how both effects can be exploited to isolate and assign the contributions from multiple isomers to the IR spectrum. The present results exemplify the sensitivity of the structure of vanadium oxide clusters on small perturbations in their environment.

MO 21.3 Thu 16:30 Poster.IV

Experimental setup for stereoselective and enantioselective cluster catalysis — ●KATHRIN LANGE, BRADLEY VISSER, MARTIN TSCHURL, ULRICH BOESL, and ULRICH HEIZ — Lichtenbergstr.4, 85748 Garching

This work describes the design and construction of a vacuum system to produce, characterise and perform reactions with chiral gas phase metal clusters. It is believed that any produced population of chiral metal clusters will be a racemic mixture of both enantiomers. Thus a method to enable the identification of enantiomers must be implemented. In the current experiment this will be attempted through the introduction of a gas phase enantiopure chiral molecule into the cluster source from a second pulsed nozzle. The added molecule will bind to the metal cluster enantiomers with varying degrees of strength and thus may be probed by either vibrational (REMPI) or dissociation spectroscopy.

MO 21.4 Thu 16:30 Poster.IV

Thermalization of cluster ions in a radio frequency ion trap — RAPHAEL PRÄG, ADAM PIECHACZEK, and BERND V. ISSENDORFF — Fakultät für Mathematik und Physik, Universität Freiburg, Stefan-Meier Str.19, 79104 Freiburg

Calorimetric studies of free, size-selected cluster ions are performed in our group. Charged clusters are temperature controlled, transferred into high vacuum, mass-selected, and photo-fragmented by a laser pulse. The recorded fragment mass spectra are sensitive to the inner energy of the thermalized clusters, which allows us to link temperature and energy and thus deduce caloric curves. In the past a temperature controlled flow tube was used for the thermalization of the clusters. After replacing it with an radio frequency ion trap, it was important to make sure that the ions are fully thermalized in the trap. The thermalization time of water cluster ions in the radio-frequency ion-trap is examined by trapping the ions for different defined intervals before they are photo-fragmented and the fragments are analyzed. This was carried out for two different temperatures of the heat bath and the experimental results are compared to a simulation.

MO 21.5 Thu 16:30 Poster.IV

Structure of Small Terbium Clusters from Far-IR Vibrational Spectroscopy — JOHN BOWLAN¹, DANIEL HARDING¹, ALEX WOODHAM¹, JEROEN JALINK², ANDREI KIRILYUK², ANDRÉ FIELICKE¹, and GERARD MEIJER¹ — ¹Fritz-Haber-Institut der Max Planck Gesellschaft, Berlin, Germany — ²Radboud University of Nijmegen, Nijmegen, The Netherlands

Understanding the remarkable magnetism of lanthanide clusters requires knowledge of their geometric structures [1]. Far-IR vibrational spectroscopy using a free electron laser is now a well developed method for structural characterization of transition metal and semiconductor clusters. However, obtaining structural assignments from IR spectra requires effective theoretical methods for finding candidate structures and accurately calculating their spectra to compare with experiment. Clusters of lanthanide metals are widely regarded as a major challenge for theory because of their open, highly localized atomic 4f shells. We present the vibrational spectra of cationic terbium clusters, and demonstrate that the Far-IR spectra can be accurately calculated using DFT with a 4f-in-core pseudopotential.

[1] Bowlan et. al. J. Appl. Phys. 107 09B509 (2010)

MO 21.6 Thu 16:30 Poster.IV

Measuring the electronic and optical properties of metal cluster-diamondoid hybrid systems: preliminary considerations and planning — TORBJÖRN RANDER¹, ROBERT RICHTER¹, ANDRE KNECHT¹, THOMAS MÖLLER¹, and TOBIAS LAU² — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstraße 36, D-10623 Berlin, Germany — ²Institut für Methoden und Instrumentierung der Forschung mit Synchrotronstrahlung, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, G-12, Albert-Einstein-Straße 15, 12489 Berlin, Germany

Here, we present the results of a pre-study and the conceptual design of an experiment to perform photoabsorption and photoluminescence measurements on size selected metal cluster-diamondoid complexes.

Such systems are of major interest in a wide range of areas, for example nano-electronics (band gap tuning, negative electron affinity materials). The planned experimental set-up will allow for in-house measurements with an OPO UV laser system as well as for measurements with other sources of excitation (e.g. synchrotron radiation from a storage ring or a FEL).

MO 21.7 Thu 16:30 Poster.IV

Vibrational spectroscopy of isolated Single Molecule Magnets (SMM) of Dy and Mn/Ni — FABIAN MENGES¹, YEVGENIY NOSENKO¹, CHRISTOPH RIEHN¹, PETER ROESKY², and GEREON NIEDNER-SCHATTEBURG¹ — ¹Fachbereich Chemie und Forschungszentrum Optimas, TU Kaiserslautern, 67663 Kaiserslautern, Germany — ²Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT), 76131 Karlsruhe, Germany

A combination of mass spectrometric and spectroscopic techniques was applied to determine the structure of newly synthesized Single Molecule Magnets (SMM) containing transition metals and lanthanides. This methodology gives insight into the binding motifs leading to cooperative effects between the metal ions. We present here work in progress of IR-MPD spectroscopy, H/D exchange reactions, energy-resolved collision induced dissociation and theoretical studies

(DFT) on DyMn₂ and DyNi₂ containing metal-organic clusters.

The grouping of high spin state transition metals (3d ions) with high magnetic anisotropic lanthanides (4f ions) could lead to single molecule magnetic behavior. However, the overall symmetry imposed by the molecular binding motifs can in fact play a key role in governing this behavior. The cooperativity of the metal centers depends on their spatial arrangement, i.e. the structure of the metal-organic cluster. Results for structural determination in the solid phase and the gas phase will be compared.

MO 21.8 Thu 16:30 Poster.IV

Fragmentation von massenselektierten Heliumclustern in starken Laserfeldern — JÖRG VOIGTSBERGER¹, JASPER BECHT¹, NADINE NEUMANN¹, MAKSYM KUNITSKI¹, HONG-KEUN KIM¹, MARKUS WAITZ¹, FLORIAN TRINTER¹, RUI A. COSTA-FRAGA¹, STEFAN ZELLER¹, ANTON KALININ¹, JIAN WU¹, ACHIM CZASCH¹, OTTMAR JAGUTZKI¹, LOTHAR PH. SCHMIDT¹, WIELAND SCHÖLLKOPF², BUM S. ZHAO², TILL JAHNKE¹ und REINHARD DÖRNER¹ — ¹Institut für Kernphysik, Goethe Universität, Frankfurt a. M., Germany — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Mit Hilfe eines Nano-Gitters konnte in einem gekühlten Helium-Gasjet aufgrund der Materiewellebeugung eine Trennung der verschiedenen Clustergrößen erreicht werden. Der hieraus resultierende, reine Dimer bzw. Trimer Jet wurde mit einem Femtosekunden-Laser ionisiert und mit der ColTRIMS-Technologie impulsspektroskopisch untersucht. Diese Methode bietet erstmals die Möglichkeit einzelne Dimere bzw. Trimere auf ihre Struktur und Größe zu untersuchen und Diskrepanzen in Theorie und Experiment zu klären.

MO 21.9 Thu 16:30 Poster.IV

Photoluminescence of Diamondoids with sp²-Impurities — ROBERT RICHTER¹, TORBJÖRN RANDER¹, TOBIAS ZIMMERMANN¹, ANDRE KNECHT¹, CHRISTOPH HEIDRICH¹, ANDREA MERLI¹, PHILLIP REISS², ARNO EHRESMANN², and THOMAS MÖLLER¹ — ¹Technische Universität Berlin, Institut für Optik und Atomare Physik, Eugene-Wigner-Building, Hardenbergstrasse 36, D-10623 Berlin — ²Institut für Physik Universität Kassel, Heinrich-Plett-Straße 40, D-34109 Kassel

Nanodiamonds, so called diamondoids are carbon clusters with perfect bulk diamond structure and complete hydrogen passivation. In previous studies we could show that certain diamondoids luminesce in the deep UV. Only recently a new class of diamondoids have been synthesized where one or more C-C-bonds exhibit sp²-hybridization. These deviations from the diamond structure can be seen as sp²-impurities which alter the overall electronic structure of the diamondoid. Absorption, photoluminescence and excitation spectra show that tuning of the optical properties by deliberate introduction of these impurities is possible.

MO 21.10 Thu 16:30 Poster.IV

Supersonic beams of neutral and ionic CO₂ clusters — BOGAUN CHEN, MONA KOSITZKI, KLAUS RADEMANN, and WOLFGANG CHRISTEN — Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489 Berlin

The formation and growth of clusters in the gas phase is of fundamental relevance. Recent progress in experimental techniques¹⁻³ and the advanced thermodynamic analysis of velocity distributions of supersonic jets^{4,5} permit an improved comprehension of these condensation processes.

We present a comprehensive investigation of CO₂ cluster beams from sub- to supercritical source densities, covering cluster sizes from 3×10^2 to 3×10^5 molecules per particle. In particular we report on the change (both increase and decrease) of the flow velocity with source density, the effect of source temperature on translational cooling, and compare the results for neutral and charged clusters.

¹W. Christen, T. Krause, K. Rademann, *Rev. Sci. Instrum.* **78**, 073106, 2007.

²W. Christen, T. Krause, B. Kobin, K. Rademann, *J. Phys. Chem. A* **115**, 6997, 2011.

³K. Luria, W. Christen, U. Even, *J. Phys. Chem. A* **115**, 7362, 2011.

⁴W. Christen, K. Rademann, *Phys. Scr.* **80**, 048127, 2009.

⁵W. Christen, K. Rademann, U. Even, *J. Phys. Chem. A* **114**, 11189, 2010.

MO 21.11 Thu 16:30 Poster.IV

Advances in imaging of ion molecule reactions — RICO

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In our group we have developed a crossed beam velocity map imaging apparatus to study ion molecule reactions. Here we report our studies on the influence of microsolvation in the reaction $\text{OH}^{\cdot} \cdot (\text{H}_2\text{O})_n + \text{CH}_3\text{I}$. Implementation of a multipole radio frequency ion trap allows us to prepare different anion water clusters in well defined initial states. Varying the collision energies between 0.5 - 2 eV reveals several reaction channels and a comparison with theoretical calculations leads to the conclusion that geometric effects play an important role in these reactions. We will also present the parametric characterization of spatial imaging (SMI) technique using laser and ion beams. A spatial resolution of less than 5 μm as well as 3D- SMI detection have been achieved and possible applications will be discussed. Finally, we will present initial plans for scattering of vibrationally excited CH_3I molecules and for dynamical studies of astrophysically relevant reactions, e.g. $\text{CO} + \text{H}_3^+$.

MO 21.12 Thu 16:30 Poster.IV

Enhanced production of low energy electrons by alpha particle impact — •HONG-KEUN KIM, JASMIN TITZE, MARKUS SCHÖFFLER, FLORIAN TRINTER, MARKUS WAITZ, JÖRG VOIGTSBERGER, HENDRIK SANN, MORITZ MECKEL, CHRISTIAN STUCK, UTE LENZ, MATTHIAS ODENWELLER, NADINE NEUMANN, SVEN SCHÖSSLER, KLAUS ULLMANN-PFLEGER, BIRTE ULRICH, RUI COSTA FRAGA, NIKOS PETRIDIS, DANIEL METZ, ANNIKA JUNG, ROBERT GRISENTI, ACHIM CZASCH, OTTMAR JAGUTZKI, LOTHAR SCHMIDT, TILL JAHNKE, HORST SCHMIDT-BÖCKING, and REINHARD DÖRNER — Goethe-Universität Frankfurt, Institut für Kernphysik, Frankfurt, Germany

Fragmentation processes after double ionization of Ne_2 by (650 keV) He^+ impact were studied. We report on the observation of Interatomic Coulombic Decay in ion-dimer collisions and show differences in the electron energy distribution of molecular and atomic Ne. A significant increase in the production of low energy (0-2 eV) electrons was detected. The experiment was performed at the 2.5 MeV Van-de-Graaff accelerator in the Institut für Kernphysik of the Goethe Universität in Frankfurt. The ionic fragments of the ionized neon dimers and atoms and at least one electron were measured in coincidence with the signal of the pulsed projectile beam in a COLTRIMS reaction microscope. Here the charged particles are guided onto delay line detectors by electrical and magnetic fields. Measuring the times of flight and the positions on the detectors allows the reconstruction of the 3-dimensional momentum vector of all measured particles.

MO 21.13 Thu 16:30 Poster.IV

The impact of pump-probe geometries on excitation dynamics in high absorbing materials — •SERGEJ BOCK, SEBASTIAN EICKE, VOLKER DIECKMANN, KRISTIN SPRINGFELD, and MIRCO IMLAU — Department of Physics, University of Osnabrück, Germany

Photoswitchable ruthenium sulfoxides like $[\text{Ru}(\text{bpy})_2(\text{OSO})]^+$ (OSO: 2-methylsulfinylbenzoate) offer a light-induced linkage isomerization located at the SO-ligand resulting in a tremendous photochromism. Studies regarding the photochromism and the kinetics of the generation and relaxation of the light-induced metastable isomers draw out an impact of the pump-probe geometry on the excitation dynamics, that arise from the pronounced pump-beam absorption.

This contribution focuses on the geometry impacts and we present a model that can describe the affected excitation dynamics. The model will be confirmed by geometry dependent measurements of excitation dynamics on the basis of the mentioned photoswitchable ruthenium sulfoxide by pump-probe technique. The simultaneous signal detection via Si PIN diodes and via a CCD line allow for measuring the dynamics parallel and perpendicularly to the direction of pump beam propagation as well as spatially resolved. This measurements offer a deep insight in the impact of the pump-probe geometries on the excitation dynamics. The contribution show up the reasons for the geometry impacts, a solution to avoid those impacts as well as the adaptability of the model to other high absorbing materials.

*Financial support: DFG (INST 190/137-1) and DAAD (50445542).

MO 21.14 Thu 16:30 Poster.IV

Optical switching of an organic photochromic triad: Demonstration of an optical gate — •MARTTI PÄRS¹, MICHAEL GRADMANN¹, REGINA SCHMIDT¹, CHRISTIANE HOFMANN¹, KATJA GRÄF², PETER BAUER², MUKUNDAN THELAKKAT², and JÜRGEN KÖHLER¹ — ¹Experimental Physics IV, University of Bayreuth, 95440 Bayreuth, Germany — ²Applied Functional Polymers, University of Bayreuth, 95440 Bayreuth, Germany

We demonstrate the operation of an optical gate by using an organic triad, that consists of a photochromic unit (dithienylcyclopentene, DCP) and two highly efficient fluorophores (perylenebisimide, PBI). The DCP can be reversibly interconverted between two bistable forms by light, leading to a strong modulation of the fluorescence intensity of PBI moieties as a function of the state of the DCP. Hence the DCP unit acts as a gate (triggered by few photons), that controls the flow of many fluorescence photons from the PBI. We will discuss the performance of the triad (modulation depth of the fluorescence, fatigue resistance and quantum yield) from the viewpoint of an optical transistor.

Reference: M. Pärs, C.C. Hofmann, K. Willinger, P. Bauer, M. Thelakkat, J. Köhler, *Angew. Chem. Int. Ed.* 2011, 50, 11405-11408

MO 21.15 Thu 16:30 Poster.IV

Electronic excitation spectra of the $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ photosensitizer bound to small silver clusters Ag_n ($n=1-20$) — OLGA BOKAREVA, •SERGEY BOKAREV, and OLIVER KÜHN — Institut für Physik, Universität Rostock, Rostock, Deutschland

Combination of metal nanoparticles with molecular adsorbates like organic dyes, semiconductors, and J-aggregates is well-known and a prospective way to design and tune functional properties of new nano-scaled materials. We present a computational study of the electronic spectra of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ (IrPS) bound to small silver clusters Ag_n ($n=1-20$). The focus on the particular Ir(III) complex is related to the developed effective photocatalytic system for water splitting combining IrPS with a sacrificial reductant and a water reduction iron catalyst [1].

We have shown that the interaction of IrPS and Ag_n leads to weak physisorption. For the systems with odd number of silver atoms, a "redox" nature of the ground electronic state: $\text{IrPS}^0 \cdots \text{Ag}_n^+$ was found, causing different directions of charge-transfer (CT) in the lowest electronic transitions of systems with odd and even number of silver atoms. The intermolecular long-range CT electronic states between IrPS and Ag_n appear in absorption spectra, which might favour further photochemical and photophysical processes involving low excited states. However, depending on the relative rates of intersystem crossing, internal conversion, and energy dissipation on the cluster particle strong quenching of photoprocesses can also happen.

[1] F. Gärtner et al. *Angew. Chem. Int. Ed.* 2009, V. 48, P. 9962.

MO 21.16 Thu 16:30 Poster.IV

Double-Auger Emission of Carbon Monoxide following Core-Excitation and Ionization — •FLORIAN TRINTER¹, MARKUS S. SCHÖFFLER¹, TILL JAHNKE¹, IRINA A. BOCHAROVA², ARNO VREDENBORG¹, FELIX P. STURM², NADINE NEUMANN¹, KYRA COLE¹, JOSHUA B. WILLIAMS⁴, MARC SIMON³, ALLEN LANDERS⁴, THORSTEN WEBER², HORST SCHMIDT-BÖCKING¹, and REINHARD DÖRNER¹ — ¹Institut für Kernphysik, Goethe-Universität Frankfurt am Main, D-60438 Frankfurt, Germany — ²Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA — ³Physics Department, Auburn University, Auburn, Alabama 36849, USA — ⁴Laboratoire de Chimie Physique Matière et Rayonnement, UPMC Université Paris 06, F-75005 Paris, France

We have studied double Auger decay after $\text{C}1s \rightarrow 2\pi^*$ core-level photo excitation (287.4 eV photons) and after ionization (306 eV) using synchrotron radiation in gas phase carbon monoxide. In this experiment the aim is to understand the dissociation pathways during the Auger decay and the photo-electron valence-electron correlation. This is a fundamental correlation yet unexplored, which plays an important role in the understanding of the energy-bond-length correlation of the shape resonance in chemical compounds. Moreover, we want to investigate the role of the initial and final state correlation as well as post collision interaction effects in the emission patterns of the outgoing electrons and thus hunt for a breakdown of the widely accepted 2-step mechanism in small molecules. New results especially on photo electron and Auger electron angular distributions will be presented and discussed.

MO 21.17 Thu 16:30 Poster.IV

Electron diffraction self imaging of molecular fragmentation

in two step double ionization of water — ●HENDRIK SANN¹, TILL JAHNKE¹, TILO HAVERMEIER¹, KATHARINA KREIDI¹, CHRISTIAN STUCK¹, MORITZ MECKEL¹, MARKUS SCHÖFFLER¹, NADINE NEUMANN¹, ROBERT WALLAUER¹, STEFAN VOSS¹, ACHIM CZASCH¹, OTTMAR JAGUTZKI¹, THORSTEN WEBER², HORST SCHMIDT-BÖCKING¹, SHUNGO MIYABE², DANIEL J. HAXTON², ANN E. OREL³, THOMAS N. RESCIGNO², and REINHARD DÖRNER¹ — ¹Institut für Kernphysik, Goethe-Universität, Max-von-Laue-Straße 1, 60438 Frankfurt am Main, Germany — ²Lawrence Berkeley National Laboratory, Chemical Sciences and Ultrafast X-ray Science Laboratory, Berkeley, California 94720, USA — ³Department of Applied Science, University of California, Davis, CA 95616, USA

We doubly ionize H₂O by single photon absorption at 43 eV leading to H⁺ + OH⁺. A direct double ionization and a sequential process in which single ionization is followed by rapid dissociation into a proton and an autoionizing OH* is identified. The angular distribution of this delayed autoionization electron shows a preferred emission in the direction of the emitted proton. This anisotropy can be reproduced almost exactly with a simple classical scattering simulation. From this simulation we obtain an internuclear distance of 800 a.u. at which the autoionization occurs.

This scattering effect should be rather general and should occur whenever a positively charged fragment is emitted from a molecule or cluster and at a later time electrons are emitted.

MO 21.18 Thu 16:30 Poster.IV

Experimental calibration of a 3D Velocity map imaging setup using HBr photodissociation — ●MIKHAIL PORETSKIY, MAIK VECKENSTEDT, CHRISTOF MAUL, and KARL-HEINZ GERICKE — Institute für Physikalische und Theoretische Chemie, Braunschweig, Deutschland

To solve the problem of the overlap of laser beams in space the HBr photodissociation can be analyzed. In a one color experiment HBr is photolyzed at a wavelength of 243.12 nm, which is also used for [2+1]-REMPI of resulting H-atoms. The distribution of the velocity vector of the produced H atoms is presented by two concentric spheres, which correspond to two channels of measured H atoms, which are different due to the spin orbit state of the bromine partner fragment Br and Br*. In two color experiment the fact that HBr can be photolyzed both at the REMPI detection wavelength 243.12 nm and at 193 nm (excimer laser) was used. The H atoms produced by both wavelengths are subsequently ionized only by 243.12 nm radiation. As a result two new channels of H atoms are observed in the velocity distribution by new spheres, which are sensitive to the position of the excimer laser beam. The position of the excimer laser beam is changed until it is overlapped with the beam of dye laser. In case of the overlap of both laser beams in space the spheres, which appears in two color experiment have to be concentric with these from the one color experiment.

MO 21.19 Thu 16:30 Poster.IV

3D velocity mapping of the Hydrogen atom formation from the 193 nm photodissociation of borazine via (2+1)-REMPI — ●MAIK VECKENSTEDT, MIKHAIL PORETSKIY, CHRISTOF MAUL, and KARL HEINZ GERICKE — Institut für Physical and Theoretical Chemistry, University Braunschweig, Germany

The kinetic energy release and the spatial distribution of the Hydrogen atom formation from the 193nm photodissociation of borazine, B₃N₃H₆, was studied by 3D velocity map imaging (VMI) setup. The excitation of borazine with 193nm and the following dissociation yields mainly in the production of the B₃N₃H₅ and H atoms. In a two-laser experiment borazine was first excited with 193nm and the generated Hydrogen atoms were ionized through a (2+1)-REMPI process at 243nm. The 3D velocity vector of individual H atom fragments was detected with a time and position sensitive delay line detector. With this technique we received the Time-of-Flight mass spectrum and the spatial distribution for this H atoms formation.

The speed distribution of the H atoms is very board and because of the relative small energetic difference between the N-H (3,94eV) and B-H (4,26eV) bonding, one cannot clearly distinguish between the contribution of these two bonds. Moreover we observed an isotropic distribution of the Hydrogen atoms and a long lifetime of the excited borazine molecule. The spatial distribution obtained by 3D VMI corroborates the previous notion of the 193nm photodissociation process. Thus the Hydrogen atom formation is not a direct photodissociation, but more likely a predissociation.

MO 21.20 Thu 16:30 Poster.IV

ESIPT in isolated hydroxychromones: Analysis by combined IR/UV spectroscopy — MARTIN WEILER, ALEXANDER BRÄCHER, ●ANKE STAMM, KRISTINA BARTL, and MARKUS GERHARDS — TU Kaiserslautern, Physikal.&Theoret. Chemie, 67663 Kaiserslautern

Photochemical reactions are of interest due to their importance in chemical and biological processes. Combined double, triple and partly quadruple resonance IR/UV spectroscopic techniques in molecular beam experiments in combination with (TD-) DFT calculations are very powerful tools to analyze photochemically induced reaction coordinates yielding direct structural information on the electronic ground and electronically excited states. We applied different combined mass- and isomerselective IR/UV and IR/IR techniques on the isolated and photochemically reactive 3-hydroxychromone (3-HC). By comparing the IR spectra of the electronic ground and an electronically excited state (S1) with (TD-)DFT calculations a proton transfer reaction after electronic excitation was verified and the resulting geometry can be identified. These findings are compared with observations for 3-hydroxyflavone and 2-(2-naphthyl)-3-hydroxychromone which differ from 3-hydroxychromone by substitutions. Especially the different life times of the molecules and their clusters with water in the first electronically excited state require the use of the large variety of combined IR/UV methods in order to get correct assignments on the different species and their reaction channels. These aspects will be discussed in detail.

MO 21.21 Thu 16:30 Poster.IV

Multimode exciton-vibrational spectra of Perylene Bisimide (PBI) molecular aggregates — SERGEY POLYUTOV and ●OLIVER KÜHN — Institut für Physik, Universität Rostock, D-18051 Rostock, Germany

Despite an enormous amount of experimental and theoretical papers focussing on the photophysical properties of molecular aggregates (MA) [1] there are still open questions related to the behavior under varying temperature [2]. In this contribution we investigate the influence of aggregate size, excitonic interactions and exciton-vibrational coupling [3] on absorption and emission spectra of PBI aggregates.

We have studied the multimode electron-vibrational absorption and emission spectra of a PBI monomer and dimer in the region of 600nm. The spectrum was calculated using an exact multimode approach based on explicit treatment of dominating vibrational modes with the largest Huang-Rhys factors [4]. The calculated energy positions and relative intensities of vibrational peaks well reproduce the experimental spectra [2]. It is shown that changing of temperature of MA may results in a change of aggregate type.

[1] O. Kühn, S. Lochbrunner, *Semicond. Semimetals* 85, 47 (2012)

[2] S. Wolter, Diploma thesis, Universität Rostock (2011)

[3] S. Polyutov, O. Kühn, T. Pullerits, *Chem. Phys.* (2012)

[4] S. Polyutov, I. Minkov, F. Gel'mukhanov, H. Ågren, *J. Phys. Chem. A* 109, 9507 (2005).

MO 21.22 Thu 16:30 Poster.IV

Solvated electrons at the water - vacuum interface — FRANZISKA BUCHNER, HANS-HERMANN RITZE, THOMAS SCHULTZ, and ●ANDREA LÜBCKE — Max-Born Institut Berlin

Solvated electrons play an important role in solution chemistry and have been extensively studied by means of transient absorption. As solvated electrons are very reagent, their behaviour at interfaces is of special interest. We use time-resolved liquid jet photoelectron spectroscopy (TRPES) at low kinetic energies to explore the energetics and dynamics of solvated electrons at the liquid surface. First, we will show, that contrary to previous assumptions, TRPES is surface sensitive. Then we will discuss the solvated electron energetics and dynamics in different environments and for different generation processes. E. g. the excitation of an alkali halide aqueous solution with sub-20 fs, 160 nm pulses leads to the formation of a solvated electron above the liquid surface which is stabilized by the cation. Its binding energy is about 2.5 eV and its lifetime is about 300 fs.

MO 21.23 Thu 16:30 Poster.IV

High Resolution IR Spectroscopy of Benzene Monomer and Dimer at Ultracold Temperature — ●SARAH GRÜN, TORSTEN POERSCHKE, and DANIEL HABIG — Ruhr-University Bochum, Bochum, Germany

$\pi \cdots \pi$ and $\text{CH} \cdots \pi$ interactions are of special interest concerning stabilization mechanisms in DNA or proteins. Therefore, benzene, as the smallest aromatic molecule, and its dimer was used as a model

and starting point for theoretical and experimental studies in the last decades. Our measurements were carried out using a high power *cw*-IR-OPO in combination with a helium nanodroplet spectrometer. We obtained IR spectra of benzene and benzene dimer in the C-H-stretching region of 3000-3110 cm^{-1} . From the pressure dependence of IR-spectra, we assigned benzene monomer as well as dimer bands. The latter, we assigned to the tilted T-shaped (TTS) structure based on comparative treatment of the experimental results with theoretical predictions as well as gas phase studies from other groups. Parallel-displaced (PD) and perfect T-shaped (PTS) structure were not observed in this frequency region. In addition, we found a splitting of the $\nu_8 + \nu_{19}$ combination band for benzene monomer, which was not splitting in gas phase matrices. This can be explained with an additional Fermi resonance coming from the helium matrix.

MO 21.24 Thu 16:30 Poster.IV

IR-spectroscopy of glycine in helium nanodroplets — ●MELANIE LETZNER, SARAH GRÜN, GERHARD SCHWAAB, and MARTINA HAVENITH — Ruhr University Bochum, Germany

Glycine is the smallest amino acid, and therefore it is of special interest as a model and starting point for theoretical and experimental studies. Whereas the crystalline form of glycine consists of zwitterions $\text{NH}_3^+ - \text{CH}_2 - \text{COO}^-$, gas phase glycine is known to exist in the non-ionized form $\text{NH}_2 - \text{CH}_2 - \text{COOH}$. The interaction between glycine and water has been widely studied using a large variety of theoretical methods. Depending on the theoretical level used, a stabilisation of the zwitterionic form is predicted for complexes containing from 2 to 7 water molecules. In low-temperature Ar matrices a set of characteristic IR absorption bands for the zwitterionic form has been observed. The higher stoichiometry complexes (glycine) $\cdots (\text{H}_2\text{O})_n$ with n larger than 3 are demonstrated to be zwitterionic H-bonded complexes. The multitude of conformations expected for these glycine-water complexes makes a combination of low temperature and high resolution spectroscopy essential. We want to use the advantages of our experiment to investigate glycine and its complexes with water in helium-nanodroplets at ultracold temperatures in the range from 3000-3800 cm^{-1} . Our measurements were carried out using a high power IR-OPO (*cw*: 2.7 W) as radiation source and a helium nanodroplet spectrometer. Helium-nanodroplets are formed by expansion of helium at 55 bar through a 5 μm nozzle which is kept at a temperature of 16 K. The status of the project is presented.

MO 21.25 Thu 16:30 Poster.IV

New apparatus for laser and XUV ionization studies of doped helium nanodroplets — ●DOMINIC BUCHTA¹, SIVA KRISHNAN², ROBERT MOSHAMMER², FRANK STIENKEMEIER¹, and MARCEL MUDRICH¹ — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg im Breisgau — ²Max Planck Institut für Kernphysik, Saupfercheckweg 1, D-69117 Heidelberg

The ionization dynamics of atomic clusters in intense ultrashort laser pulses has been an active area of research in recent years at near-infrared (NIR), vacuum-ultraviolet, and soft x-ray wavelengths [1-3]. Doped He nanodroplets are particularly interesting heterogeneous systems due to extremely different masses and ionization energies of guest and host atoms as well as due to the peculiar quantum properties of He nanodroplets. We present a new mobile and versatile apparatus for producing beams of doped He nanodroplets that will be employed for strong-field ionization studies using few-cycle laser pulses as well as for synchrotron and FEL experiments.

[1] A.Mikaberidze et al., Phys.Rev.Lett. 102, 128102 (2009)

[2] S.R. Krishnan et al., Phys.Rev.Lett. 107, 173402 (2011)

[3] D.S. Peterka et al., J.Phys.chem. A 2007, 111, 7449-7459

MO 21.26 Thu 16:30 Poster.IV

Probing doped helium nanodroplets with amplified femtosecond laser pulses — ●MANUEL ROMETSCH, BARBARA GRÜNER, AMON SIEG, FRANK STIENKEMEIER, and MARCEL MUDRICH — Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany

Superfluid helium nanodroplets doped with atoms and molecules are intriguing systems at the border between gas-phase and condensed matter physics. We present experiments on the photoionization of doped helium nanodroplets using different femtosecond lasers, ranging from a high-repetition rate (80 MHz) Ti:Sa oscillator in the NIR to an amplified low-repetition rate (5 kHz) OPA-system covering wavelengths from the NIR to the UV. One- and two-color pump-probe schemes are applied in combination with photoion and photoelectron

detection. This gives access to a wide spectrum of dynamical phenomena, such as the desorption off the droplet surface and alkali-helium exciplex formation [1], droplet induced relaxation [2], as well as the ignition of a nanoplasma [3].

[1] Mudrich et al., Phys. Rev. Lett. 100, 023401 (2008)

[2] Grüner et al., PCCP 13, 6816 (2011)

[3] Krishnan et al., Phys. Rev. Lett.107, 173402 (2011)

MO 21.27 Thu 16:30 Poster.IV

Infrared spectroscopy of small molecules inside helium nanodroplets using a narrow-linewidth VECSEL — ●MICHAEL RICHTER¹, SEBASTIAN KASPAR², MARCEL RATTUNDE², MARKUS MÜLLER¹, JOACHIM WAGNER², and FRANK STIENKEMEIER¹ — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg im Breisgau — ²Fraunhofer-Institut für Angewandte Festkörperphysik, Tullastrasse 72, 79108 Freiburg im Breisgau

We are presenting a setup to perform spectroscopy of small molecules like CO_2 , CO or H_2O by using a tuneable, single mode operating VECSEL (Vertical External Cavity Surface Emitting Laser)¹. The laser system provides narrow-linewidth operation (<10kHz) and still delivers a reasonable output power in the region of 100mW to obtain absorption spectra with high resolution. We will focus on IR vibrational overtone spectroscopy in the 1.9 to 2.3 μm wavelength range. Further on we plan to probe these molecules inside helium nanodroplets to study the interaction with the ultra cold (370mK) and superfluid matrix. In particular one expects relevant information on reduced rotational constants and the role of a normal fluid fraction in the vicinity of the dopant molecule.

¹ B. Rösener et al., Optics Letters Vol. 36, No. 18, 3587 (2011)

MO 21.28 Thu 16:30 Poster.IV

Fluorescence emission spectroscopy of PTDCDA in helium droplets — ●LUKAS SCHÄFER, MARKUS MÜLLER, MATTHIEU DVO-RAK, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Helium nanodroplet isolation (HENDI) spectroscopy has become a well-established technique for studying atoms, molecules and their complexes. The physical properties of helium droplets such as their low temperature (380mK), the weak interactions with atoms and molecules, and the superfluid property make them a favorite matrix for spectroscopy. We apply HENDI to investigate the emission spectra of PTDCDA molecule and its complexes. PTDCDA (3,4,9,10 perylene tetracarboxylic dianhydride) with its semiconducting properties is a promising material for organic device applications in light-emitting diodes and photovoltaics. Emission spectra of dimers and oligomers attached to helium nanodroplets provide insight into the vibrational structure of the electronic ground state and the first electronically excited state. Moreover, one gets information on the inter-molecular coupling and its dynamics.

MO 21.29 Thu 16:30 Poster.IV

Detection of photoelectrons for helium nanodroplet spectroscopy of organic molecules — ●FABIAN HOHNLOSER, MARKUS MÜLLER, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Electronic spectroscopy of molecules in helium nanodroplets has been exploited applying a variety of detection techniques including fluorescence, droplet beam depletion or ionization processes. In ionization experiments the detection of ions can be hampered when the ions remain attached to the droplet and very large masses have to be detected. We study the option of a simple and efficient setup of detecting photoelectrons in order to do resonance enhanced multiphoton ionization (REMPI) spectroscopy. In comparison with laser-induced fluorescence methods, in particular non-radiative processes of larger organic molecules can be probed in this way.

MO 21.30 Thu 16:30 Poster.IV

Laser ablation as a method for doping helium nanodroplets — ●MARTIN SINGER, RAPHAEL KATZY, and FRANK STIENKEMEIER — Universität Freiburg, Physikalisches Institut, 79104 Freiburg, Germany

Helium nanodroplet isolation has been proven to be a versatile method for spectroscopy at temperatures below 1K [1]. The variety of dopants to be loaded into the droplets depends crucially on available methods for producing atoms and molecules in the gas phase for the pick-up process. Besides gas cells and ovens also laser ablation has been established as a method for doping both fragile organic molecules and

refractory metals [2].

A pulsed droplet source provides great advantages compared to a continuous beam in terms of gas load and droplet density. The inherently pulsed laser ablation source has so far only been used with continuous helium droplet sources. For the Low Density Matter end-

station at the FERMI XUV free electron laser, we will combine a pulsed droplet source with a laser ablation setup. The design of the setup will be presented.

[1] J.P. Toennies, A.F. Vilesov, *Angew. Chem.* 43 (2004) 2622

[2] M. Mudrich et al., *Rev. Sci. Instr.* 78, 103106 (2007)

MO 22: Cluster

Time: Friday 10:30–12:00

Location: V38.02

MO 22.1 Fri 10:30 V38.02

Isomer-Selective IR/IR Double Resonance Spectroscopy: Isolating the Spectral Signatures of $H^+(H_2O)_6^+$ Isomers — •NADJA HEINE¹, GIEL BERDEN², GERARD MEIJER¹, and KNUT ASMIS¹ — ¹Fritz-Haber-Institut, 14195 Berlin, Germany — ²FOM Institute, 3439 Nieuwegein, The Netherlands

Understanding how protons are hydrated remains an important and challenging research area. The anomalously high proton mobility of water can be explained by a periodic isomerization between the Eigen and Zundel binding motifs, $H_3O^+(aq)$ and $H_5O_2^+(aq)$, respectively, even though the detailed mechanism is considerably more complex. These rapidly interconverting structures from the condensed phase can be stabilized, isolated and studied in the gas phase in the form of protonated water clusters. The smallest protonated water clusters that exhibits structural isomers related to the Eigen and Zundel motifs experimentally is the protonated water hexamer $H^+(H_2O)_6^+$.

Here, we present first results on infrared/infrared (IR/IR) double resonance experiments on $H^+(H_2O)_6^+$. Protonated water clusters are formed by electrospray ionization, mass-selected, cooled to cryogenic temperatures, and messenger-tagged (H_2) in a buffer gas filled ion trap. Isomer-selective IR/IR photodissociation spectra are measured from 300-4000 cm^{-1} by combining population-labeling double resonance spectroscopy with the widely tunable IR radiation of the free electron laser FELIX. The results demonstrate that two isomers, an Eigen and a Zundel-type isomer, are indeed present and that their IR spectra can be measured individually over the complete spectral range.

MO 22.2 Fri 10:45 V38.02

Structural Variability in Transition Metal Oxide Clusters: Gas Phase Vibrational Spectroscopy of $V_3O_{6-8}^+$ — •CLAUDIA BRIEGER¹, TORSTEN WENDE¹, JENS DÖBLER², ANDRZEJ NIEDZIOLA², JOACHIM SAUER², GERARD MEIJER¹, and KNUT R. ASMIS¹ — ¹Fritz-Haber Institut der MPG, Berlin — ²Humboldt Universität Berlin

Vanadium oxides exhibit a high structural variability and redox activity which comes to play into heterogeneous catalysis. Interestingly, the structure of the active sites in vanadium oxide catalysts is often not well known. Infrared photodissociation (IRPD) spectroscopy can be used to obtain structural information on isolated clusters in the gas phase. Here, we study the structures of tri-nuclear vanadium oxide cations. IRPD spectra of $V_3O_6^+He_{1-4}$, $V_3O_7^+Ar_{0-1}$, and $V_3O_8^+Ar_{0-2}$ from 350 to 1200 cm^{-1} are presented. $V_3O_7^+$ and $V_3O_8^+$ have a cage-like structure whereas a chain isomer is found to be most stable for $V_3O_6^+$. The binding of the rare gas atoms to $V_3O_{6-8}^+$ clusters is found to be strong, up to 58 kJ/mol for Ar, and markedly isomer-dependent, resulting in two interesting effects. First, for $V_3O_7^+Ar_1$ and $V_3O_8^+Ar_1$ an energetic reordering of the isomers compared to the bare ion is observed, making the ring-motif the most stable one. Second, different isomers bind different number of rare gas atoms. We demonstrate, how both effects can be exploited to isolate and assign the contributions from multiple isomers to the IR spectrum. The present results exemplify the sensitivity of the structure of vanadium oxide clusters on small perturbations in their environment.

MO 22.3 Fri 11:00 V38.02

Activation of oxygen on small cationic platinum clusters in the gas phase — •CHRISTIAN KERPAL¹, DAN HARDING¹, ALEXANDER HERMES², SUZANNE HAMILTON², ROBERT MOFFATT², STUART MACKENZIE², GERARD MEIJER¹, and ANDRÉ FIELICKE¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin — ²Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QZ, UK

Small clusters of platinum represent model systems for potentially important industrial catalysts, e.g. for the activation of C-H bonds and for fuel cells. The long term goal of such cluster model studies is to

understand the chemistry occurring at specific low coordinated metal sites in heterogeneous catalysis. However, the properties of metal clusters often differ dramatically with particle size. As most of the physical and chemical properties of clusters are directly related to their geometries, the determination of the precise structure is essential. The combination of infrared multiple photon dissociation (IR-MPD) spectroscopy and density functional theory (DFT) calculations provides a means to get detailed knowledge of the structures of both bare metal clusters and the adsorption geometries of small ligands on the clusters. Here we present IR-MPD spectra of $Pt_nO_{2m}^+$ clusters for $n \leq 6$; $m = 1, 2$ and a comparison to DFT calculations, allowing structural determination for the cluster-ligand complexes. These structures give direct information on the activation of the oxygen, showing different types of molecular and dissociated binding and in some cases a mixture of both, depending on cluster size and oxygen coverage.

MO 22.4 Fri 11:15 V38.02

Electronic structure and binding energies of structurally modified diamondoid complexes studied with photoemission spectroscopy — •TOBIAS ZIMMERMANN¹, ROBERT RICHTER¹, DAVID WOLTER¹, TORBJÖRN RANDE¹, PETER SCHREINER², and THOMAS MÖLLER¹ — ¹Technische Universität Berlin, Institut für Optik und Atomare Physik — ²Justus-Liebig-Universität Gießen, Institut für Organische Chemie

While the smallest diamondoids, in particular Adamantane, have been known for some decades as perfectly shape- and mass-selectable carbon clusters, their significant scientific interest has risen only in the last few years. This is due to the fact that now also the larger ones have become more widely available due to new extraction and synthesis possibilities. Adamantane, with only ten carbon atoms, can be seen as the smallest unit of the macroscopic diamond crystal structure. The electronic structure of such nanoparticles can be analyzed with the help of photoemission spectroscopy (PES). In recent experiments we investigated the electronic structure of structurally modified lower diamondoids and lower diamondoid complexes. In particular we focus on lower diamondoid complexes containing sp^2 -impurities. These systems are of interest due to the fact that sp^2 -impurities in bulk diamond are known to enhance luminescence. Recently, it has also been reported that this type of structures possesses some of the longest C-C bonds known, the peculiarities of which may be studied by using PES.

MO 22.5 Fri 11:30 V38.02

Experimental and theoretical Raman analysis of functionalized diamondoids — •REINHARD MEINKE¹, ROBERT RICHTER¹, THOMAS MÖLLER¹, BORYSLAV TKACHENKO², PETER R. SCHREINER², CHRISTIAN THOMSEN¹, and JANINA MAULTZSCH¹ — ¹Institut für Festkörperphysik, Technische Universität Berlin, Germany — ²Institut für Organische Chemie, Justus-Liebig-Universität Gießen, Germany

Diamondoids functionalized with thiol, alcohol and amine groups [1] are investigated by means of Raman spectroscopy. Here we present so-called fingerprint regions in the Raman spectra which can be used for determination of functionalization in diamondoids. Several effects due to functionalization are observed: frequency shift of Raman modes, activation of Raman-inactive modes, and splitting of degenerate modes. We show how to determine the site and the type of the functional group with the help of the fingerprint regions. The Raman modes have been characterized and assigned by supporting DFT computations using Gaussian 09, using the B3LYP functional and the basis set 6-311G(d).

[1] Hartmut Schwertfeger, Andrey A. Fokin, and Peter R. Schreiner, *Angew. Chem. Int. Ed.* 2008, 47, 1022/1036. DOI: 10.1002/anie.200701684

MO 22.6 Fri 11:45 V38.02

Molecular fragmentation and charge redistribution in XeF_2

after K-shell photoionization — ROBERT W. DUNFORD¹, STEPHEN H. SOUTHWORTH¹, DIPANWITA RAY¹, ELLIOT P. KANTER¹, BERTOLD KRAESSIG¹, LINDA YOUNG¹, DOHN A. ARMS¹, ERIC M. DUFRESNE¹, DONALD A. WALKO¹, ●ORIOLE VENDRELL², SANG-KIL SON², and ROBIN SANTRA^{2,3} — ¹Argonne National Laboratory, Lemont, IL 60439, USA — ²Center for Free-Electron Laser Science, DESY, 22607 Hamburg, Germany — ³Department of Physics, University of Hamburg, 20355 Hamburg, Germany

The photoionization of an inner-shell electron in a heavy atom by synchrotron radiation sets off a cascade of x-ray and Auger transitions as the atom relaxes and reaches its final charge state. If the heavy atom is embedded in a molecule, the decay is accompanied by charge

redistribution and molecular fragmentation processes.

In this work, we investigate the effect of Xe K-shell hole in XeF₂ and compare it to the isolated atomic case, Xe. The average total charge produced for Xe is +8, whereas it is +9 for XeF₂. Such similarity suggests a model in which the cascade proceeds at the atomic level followed by charge redistribution and Coulomb explosion. Simulations of the decay cascade of Xe, however, indicate that the cascade lasts for about 100 fs, in which case nuclear motion may play a role. Moreover, energetic considerations based on an independent ion model suggest that it is unlikely that the total charge in XeF₂ is initially produced entirely on Xe. Therefore, a more complex mechanism involving molecular effects is probably at play.

MO 23: Cold Molecules III

Time: Friday 10:30–12:00

Location: V38.03

Invited Talk

MO 23.1 Fri 10:30 V38.03

A homonuclear polar molecule — ●HOSSEIN SADEGHPOUR — ITAMP- harvard-smithsonian center for astrophysics, cambridge, ma 02138

Manipulating Rydberg interactions in ultracold ensemble is currently in vogue due to the long-range nature of forces and large dipole moments. Interactions between ultracold Rydberg and ground state atoms lead for formation of exotic classes of Rydberg molecules with peculiar properties. A particular class of such molecules was recently observed in Stuttgart and was found to sport significant permanent electric dipole moment, even though that the molecules themselves were homonuclear. In this presentation, I will describe the physics of the formation of permanent dipole moments in homonuclear species, arising from symmetry breaking. The work has appeared in Science Vol. 334 no. pp. 1110-1114, 2011, in collaboration with MPIPES and Univ. of Stuttgart.

MO 23.2 Fri 11:00 V38.03

Non-local state-swapping of polar molecules in bilayers — ●A. PIKOVSKI¹, M. KLAWUNN², A. RECATI², and L. SANTOS¹ — ¹Institut f. Theoretische Physik, Leibniz Universität Hannover, Appelstr. 2, 30169, Hannover, Germany — ²INO-CNR BEC Center and Dipartimento di Fisica, Università di Trento, 38123 Povo, Italy

The observation of significant dipolar effects in gases of ultra-cold polar molecules typically demands a strong external electric field to polarize the molecules. We show that even in the absence of a strong polarization, dipolar effects may play a crucial role in the physics of polar molecules in bilayers, provided that the molecules in each layer are initially prepared in a different rotational state. Collisions due to dipolar interactions result in an exchange of the rotational state between molecules in different layers, even for weak applied electric fields. This swapping rate has a non-trivial dependence on density, temperature, inter-layer spacing, and population imbalance. For reactive molecules such as KRb, chemical recombination immediately follows a non-local swap and dominates the losses even for temperatures well above quantum degeneracy, and hence could be observed under current experimental conditions. [arXiv:1108.5642]

MO 23.3 Fri 11:15 V38.03

Vibrational excitation of polar molecules trapped on a chip — ●SILVIO MARX, MARK ABEL, GABRIELE SANTAMBROGIO, and GERARD MEIJER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Over the last decade Stark decelerators have proven to be an important tool for the manipulation of external degrees of freedom of neutral polar molecules. In addition, the simultaneous manipulation of internal degrees of freedom like vibrational quantum states of neutral polar molecules is necessary to gain full control over molecular motion. Here, CO molecules are trapped over the surface of a microchip and then vibrationally excited using a narrow band infrared laser. Combined with time of flight measurements, excitation of trapped molecules al-

lows the study of quantum-state-dependent trap strength. The ability to optically address trapped molecules shows the versatility of the chip decelerator approach. It is anticipated that future chip-based experiments, for example on chemical reactions, will greatly benefit from the ability to probe the product final state.

MO 23.4 Fri 11:30 V38.03

Depletion Stark Spectroscopy of Cold Polar Molecules in a Homogeneous Field Electric Trap — ●ROSA GLÖCKNER, BARBARA G.U. ENGLERT, MARTIN ZEPPENFELD, and GERHARD REMPE — Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, 85748 Garching

Cold molecules are expected to substantially increase the resolution in high-precision molecular spectroscopy with applications ranging from tests of quantum electrodynamics to the search for an electron electric dipole moment. For many applications, long interrogation times are essential which suggests trapping of cold polar molecules. However, broadening due to the trapping fields seems to contradict the desire to observe narrow spectral features.

Here, we present depletion spectroscopy in a novel microstructured electric trap which exhibits tunable homogeneous fields over a large fraction of the trap volume [1]. Using either infrared or mm-wave radiation allows depletion of individual rotational states with a Stark broadening of only a few percent of the trap depth, much less than the molecular temperature. A 1/e storage time of over 10 s in the trap provides for long interrogation times enabling spectroscopy of weak transitions. Future improvements will allow spectroscopy with kHz resolution establishing our experiment as a novel platform for precision spectroscopy.

[1] B.G.U. Englert *et al.*, Phys. Rev. Lett, in press (arXiv:1107.2821).

MO 23.5 Fri 11:45 V38.03

Using cold molecules to detect molecular parity violation — ●JOOST VAN DEN BERG, KLAUS JUNGMANN, CORINE MEINEMA, AERNOUT VAN DER POEL, and STEVEN HOEKSTRA — KVI, University of Groningen, The Netherlands

We combine novel experimental techniques to decelerate and cool heavy diatomic molecules, in order to detect and study molecular parity violation. Parity violation has so far never been observed in molecules. Parity-violating effects, originating from the weak interaction, are most pronounced in heavy molecules, and most accurately measured in cold samples of trapped molecules. Stark-deceleration and trapping of heavy molecules is more demanding compared to light molecules such as NH and OH. Using recent advances in Stark-deceleration we set out to decelerate and trap heavy alkaline-earth halide molecules. Initially we focus on the SrF molecule. We are currently working on a supersonic beam of SrF molecules, constructing a Stark-decelerator based on ring electrodes, and exploring the opportunities for molecular lasercooling. Possibilities to use RaF molecules are also being investigated. A new generation of precision measurements to probe fundamental interactions and symmetries is possible once such samples of sufficiently cold molecules are available.